THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 1 MARCH, 1933 NUMBER 3

On the Theory of the Structure of CH_4 and Related Molecules. Part I[1]

J. H. VAN VLECK, *Department of Physics, University of Wisconsin*
(Received December 27, 1932)

The primary purpose of the present series of papers is to give more explicit mathematical form to the theory of Mulliken and Hund, and in some instances to the alternative theories of Pauling and Slater and of Heitler and Rumer, for valence in carbon compounds. A critical comparison is given of the Slater-Pauling and Hund-Mulliken concepts of CH_4, which are based respectively on localized bonds ("electron pairs") with the Heitler-London method, and on one-electron wave functions (Mulliken's "orbitals") for a self-consistent field with tetrahedral symmetry. The H-M procedure avoids hybridization of the carbon $2s$ and $2p$ wave functions, but allows two (though never three or more) electrons to accumulate on one H atom, as well as up to eight on a C atom. Inadequate cognizance is thus taken of the tendency of inter-electronic Coulomb forces to keep two electrons apart. The S-P procedure avoids this excessive accumulation, but at the expense of not letting an individual wave function be of a symmetry type (irreducible group representation) appropriate to a tetrahedral field. In particular, its s-p hybridization "undiagonalizes" the internal energy of the C atom. These points are illustrated by explicit exhibition of the secular determinant, which is the main new feature. Because inter-electronic repulsions make the dynamical problem more complicated than a one-electron one, the tetrahedral symmetry need only be preserved in the properties of the total wave function of the entire system rather than that of one electron, but the departures from individual tetrahedral symmetry should be less than in the Slater-Pauling theory if the Hartree self-consistent field is really a good approximation. Thus both the H-M and S-P methods, though qualitatively exceedingly illuminating, have their own characteristic drawbacks from a quantitative standpoint unless refined by inclusion of higher approximations which ultimately merge the two methods but which practically are very difficult to make.

TWO approaches have been opened to the subject of directed or orbital valence[2] in polyatomic molecules. One method is that developed by Slater[3] and by Pauling.[4] Their model is based on what Hund calls a "localization" of bonds whereby particular wave functions are assigned to "overlap" particular atoms. To explain tetrahedral carbon compounds, the so-called "sp^3" valences and wave functions are introduced. Namely, Pauling and Slater show that by taking linear combinations of the usual $2s$ and $2p$ wave functions it is possible to build four orthogonal wave functions which project in space like the four corners of a tetrahedron. The Slater-Pauling model lends itself particularly to calculations by means of the Heitler-London method, in a generalized form given by Slater[3] and by Born.[5]

[1] A preliminary account was given at the Washington meeting of the American Physical Society, April, 1932, (abstract in Phys. Rev. 40, 1037 (1932)).

[2] Since we are here confining our attention to theories of directed or orbital valence, we do not need to include in the present discussion the Heitler-Rumer treatment of carbon compounds, in which the directional properties exist only in virtue of the repulsions between the atoms attached by the central carbon atom. This Heitler-Rumer method must not, however, be overlooked and will be compared with the other methods in Part III.

[3] J. C. Slater, Phys. Rev. **37**, 481; **38**, 1109 (1931).

[4] L. Pauling, J. Am. Chem. Soc. **53**, 1367, 3225 (1931).

[5] M. Born, Zeits. f. Physik **64**, 729; **65**, 718 (1930).

The other approach is that due to Hund[6] and to Mulliken,[7] and is a generalization of their diatomic configuration theory. In Mulliken's recent model, an electron is not assigned to a particular valence but is allowed to move in a field of the same symmetry as that of the molecule in question; e.g., a field of tetrahedral symmetry in CH_4. Great simplicity rests in the fact that with this model the dynamics are that of a "one electron system," for instance the two center problem in diatomic molecules, the five center one in CH_4. Electrons are, so to speak, fed to the molecule one at a time, and by the Pauli principle not more than two of them can be digested in the same orbital state. Inter-electronic repulsions can, in principle, be included to the extent to which they may be represented by a Hartree self-consistent field of the given symmetry. If the molecule is symmetrical, several solutions of the "one-electron" wave equation may have the same energy. The degree of degeneracy can be determined from that famous paper of Bethe[8] in which the different representations of the rotation group are resolved into their irreducible portions in various crystallographic groups. In particular in the tetrahedral models the two-quantum levels split in the same fashion as for a central field, *viz.*, into one isolated term (the $2s$ wave function) and one triply degenerate term (three arbitrary orthogonal linear combinations of the usual $2p$ wave functions). It is to be particularly noted that Mulliken's tetrahedral model does not demand or even allow "hybridization," i.e., intermingling of the $2s$ and $2p$ wave functions in linear combinations. The method of calculation with the Mulliken model is essentially a generalization of one devised by Hund for simple cases, and is at least superficially very different from the Heitler-London method, as we shall see. The new contribution of Mulliken's recent paper, as compared to Hund's previous work, is the qualitative consideration of the arrangement of energy levels under molecular fields of given symmetry types.

Both the Slater-Pauling and Hund-Mulliken schemes predict a right-angled model for H_2O if one neglects (a) the forces between the two H atoms, (b) the finite separation of the ^1S, ^3P, ^1D terms arising from the configuration p^4 of O, and (c) the bonding power of the two $2s$ electrons of O. This right-angled feature has already been demonstrated common to both methods in the literature, but we may here call attention to the fact that they give nearly similar energies of formation of H_2O when the constants are determined by an assumed value of the energy of OH. Namely both schemes are readily seen to yield the result that the energy of the reaction $2H+O=H_2O$ is double that of $H+O=OH$, if we neglect items (a), (b), and (c) above, also (d) interaction terms between $1s$ of H and $2p\pi$ of O, which are surely subordinate to those between $1s$ and $2p\sigma$, and (e) allowance in the Heitler-London-Slater-Pauling method for the fact that the electron pairing is imperfect, i.e., the valences not 100 percent "pure" in Weyl's sense. Slater mentions that the heat of formation of OH from O and H is probably about 5 volts, and hence both schemes agree in predicting that the heat of H_2O from O and 2H is in the neighborhood of 10 volts, in accord with experiment.[9]

Critical Comparison of Mulliken and Slater-Pauling Wave Functions: Pros and Cons of Hybridization

Our next point will be a mathematical calculation exhibiting explicitly why the s and p wave functions do not hybridize in the Mulliken model of CH_4. We shall start with a system of representation in which the sp^3 wave functions are used, and show that proper solution of the secular problem introduces a canonical transformation which destroys the hybridization. Following Hund, we shall assume that an idealized localized valence bond between an sp^3 wave function of C and a $1s$ wave function of H can be represented by using a wave function of the form $\alpha\psi(1s;\ \mathrm{H})+(1-\alpha^2)^{\frac{1}{2}}\psi(sp^3;\ \mathrm{C})$ where the axis of the sp^3 function is, of course, to be taken coincident with the C−H axis. When we use a notation such as $\psi(1s;\ \mathrm{H}_i)$ we mean a $1s$ wave

[6] F. Hund, Zeits. f. Physik **73**, 1, 565; **74**, 429 (1931–2).
[7] R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49 (1932).
[8] H. Bethe, Ann. d. Physik **3**, 133 (1929).

[9] A. S. Coolidge has recently made a calculation of H_2O by the Slater-Pauling method without the use of as many approximations as (a)−(e); (Phys. Rev. **42**, 189 (1932)). Unfortunately the accord with experiment is poor, suggesting that the close agreement achieved with the less refined calculations is perhaps somewhat accidental.

function for an H attracting center. The subscript i ($i=a, b, c, d$) is inserted only when it is necessary to distinguish between the four different H nuclei involved in CH_4. Similarly $\psi(2p; C)$ denotes a $2p$ wave function for a C attracting center, $\psi(sp^3; C)$ an sp^3 one, etc. When we come to CH_4 we can no longer hope to express the molecular wave functions as linear combinations of two wave functions, as in a diatomic problem, but instead must use linear combinations of the following eight wave functions, denoted by I–IV′

$$\left.\begin{aligned} &\mathrm{I}=\psi(1s; \mathrm{H}_a), \quad \mathrm{II}=\psi(1s; \mathrm{H}_b), \quad \mathrm{III}=\psi(1s; \mathrm{H}_c) \quad \mathrm{IV}=\psi(1s; \mathrm{H}_d); \\ &\mathrm{I}', \mathrm{II}', \mathrm{III}', \mathrm{IV}'=sp^3 \text{ wave functions of C directed along} \\ &\qquad\qquad \mathrm{C}-\mathrm{H}_a, \mathrm{C}-\mathrm{H}_b, \mathrm{C}-\mathrm{H}_c, \mathrm{C}-\mathrm{H}_d \text{ respectively.} \end{aligned}\right\} \quad (1)$$

The secular determinant is of the form

$$\begin{vmatrix} a-W & b & b & b & c-dW & e-fW & e-fW & e-fW \\ b & a-W & b & b & e-fW & c-dW & e-fW & e-fW \\ b & b & a-W & b & e-fW & e-fW & c-dW & e-fW \\ b & b & b & a-W & e-fW & e-fW & e-fW & c-dW \\ c-dW & e-fW & e-fW & e-W & k-W & g-hW & g-hW & g-hW \\ e-fW & c-dW & e-fW & e-fW & g-hW & k-W & g-hW & g-hW \\ e-fW & e-fW & c-dW & e-fW & g-hW & g-hW & k-W & g-hW \\ e-fW & e-fW & e-fW & c-dW & g-hW & g-hW & g-hW & k-W \end{vmatrix} . \quad (2)$$

The rows and columns are indexed with respect to I′, ···, IV′, I, ···, IV. The constants c, e are Hund resonance terms between the C and H atoms, and g a similar term between the H atoms themselves. By a resonance term or integral we mean a matrix element $\int \psi' \mathbf{H} \psi dv$ in which ψ', ψ are single electron wave functions for different atoms and in which $\mathbf{H}$ is the Hamiltonian operator. It is not to be confused with "exchange integrals," which have a meaning only in two-or-more electron systems and in which electrons are permuted rather than simply one electron transferred from one atom to another. The term b exists because the hybridization prevents l being a good quantum number. The energy W appears off the diagonal because the wave functions of different attracting centers are not mutually orthogonal. On the other hand the C wave functions are orthogonal to each other, and hence W does not appear off the diagonal in the upper left quarter of (2). We shall not attempt at present to express the various constants in terms of the familiar integrals of the two-center problem, but substantially this will be done in Part II in connection with more general models (cf. especially note 7 of Part II). The occurrence of the same letter in several places in (2) is, of course, a consequence of the tetrahedral symmetry and complete parity of the four sp^3 wave functions except for direction. Clearly the Hund resonance term has one value c for pairs of wave functions such as (I, I′), (II, II′)···(IV, IV′) and another common value, say e, for (I, II′), (II, I′), (I, III′), etc., while g denotes the value for H−H pairs such as (I, II), etc.

The fact that the nonvanishing off-diagonal elements of (2) are not confined to the places (I; I′), (II; II′), ···, (IV; IV′), of course, shows that localization is impossible, i.e., that twofold linear combinations of the form $\alpha \mathrm{I} + (1-\alpha^2)^{\frac{1}{2}} \mathrm{I}'$, etc., are inadequate wave functions. Great simplification can, however, be achieved by making a canonical transformation corresponding to the introduction of the eight new wave functions[10]

[10] In unpublished work, Mulliken has also independently found that the functions ψ_1, ψ_2, ψ_3, ψ_4 defined in (3) are linear combinations of the H wave functions appropriate to the tetrahedral symmetry. Mulliken's method of obtaining the combinations was a study of general symmetry properties rather than of the secular determinant. He has also thus deduced independently the trigonal wave functions to be given in Eq. (29) of Part II.

$$\begin{aligned}
&\psi_1=\tfrac{1}{2}[\mathrm{I}+\mathrm{II}+\mathrm{III}+\mathrm{IV}], \quad \psi_2=\tfrac{1}{2}[\mathrm{I}+\mathrm{II}-\mathrm{III}-\mathrm{IV}],\\
&\psi_3=\tfrac{1}{2}[\mathrm{I}-\mathrm{II}+\mathrm{III}-\mathrm{IV}], \quad \psi_4=\tfrac{1}{2}[\mathrm{I}-\mathrm{II}-\mathrm{III}+\mathrm{IV}]\\
&\psi_1'=\tfrac{1}{2}[\mathrm{I}'+\mathrm{II}'+\mathrm{III}'+\mathrm{IV}'], \quad \psi_2'=\tfrac{1}{2}[\mathrm{I}'+\mathrm{II}'-\mathrm{III}'-\mathrm{IV}'],\\
&\psi_3'=\tfrac{1}{2}[\mathrm{I}'-\mathrm{II}'+\mathrm{III}'-\mathrm{IV}'], \quad \psi_4'=\tfrac{1}{2}[\mathrm{I}'-\mathrm{II}'-\mathrm{III}'+\mathrm{IV}']
\end{aligned} \tag{3}$$

in place of $\mathrm{I}\cdots\mathrm{IV}'$. One verifies that the secular determinant then factors into four second order determinants, of which three are identical. The determinantal equations occurring once and thrice are given respectively by the upper and lower choice of sign in the following Eq. (4):

$$\begin{vmatrix} a+(b\pm 2b)-W & c+(e\pm 2e)-dW-(f\pm 2f)W \\ c+(e\pm 2e)-dW-(f\pm 2f)W & k+(g\pm 2g)-W-(h\pm 2h)W \end{vmatrix}=0. \tag{4}$$

The pairs of wave functions which are associated with the four second order determinants are respectively (ψ_1, ψ_1'), (ψ_2, ψ_2'), (ψ_3, ψ_3'), (ψ_4, ψ_4'). All but the first of these pairs are correlated with the lower choice of sign in (4). The transformation (3) which simplifies (2) to (4) completely eliminates the sp^3 hybridization, since ψ_1' does not combine with ψ_2', ψ_3', ψ_4', and since further ψ_1' is merely an ordinary $2s$ wave function. The latter statement follows from the fact that the sp^3 functions are of the form[3, 4] $\frac{1}{2}\psi(2s)+f(r)(\mathbf{r}\cdot\mathbf{1}_i)$, where $\mathbf{1}_i$ is a unit vector directed along $\mathrm{C}-\mathrm{H}_i$, whence $\mathbf{1}_a+\mathbf{1}_b+\mathbf{1}_c+\mathbf{1}_d=0$. Also ψ_2', ψ_3', ψ_4' are ordinary $2p$ wave functions.

One thing must be particularly noted. According to the ideas of Hund and Mulliken we must fill twice each of the lower roots of the four second order equations:—twice because the Pauli principle allows two electrons to a given orbital state. The total wave function for the eight electron CH_4 system is (forgetting, as we do throughout, the K shell of C)

$$\Phi_1(1)\Phi_1(2)\Phi_2(3)\Phi_2(4)\Phi_3(5)\Phi_3(6)\Phi_4(7)\Phi_4(8) \tag{5}$$

with

$$\Phi_i=\beta_i\psi_i+(1-\beta_i^2)^{\frac{1}{2}}\psi_i' \ (i=1, \cdots, 4)$$
$$\beta_2=\beta_3=\beta_4. \tag{6}$$

Here $\Phi_i(j)$ means that the coordinates involved as arguments of Φ_i relate to electron j. The values of β_1, β_2 are determined by finding the transformation matrices connected with the two secular problems (4).

Accumulation of electrons on one nucleus. If we express (5) in terms of the original functions $\mathrm{I}, \cdots, \mathrm{IV}'$ by means of (3) we see that (5) will involve terms of the form $\mathrm{I}(1)\mathrm{I}(2)\cdots\mathrm{I}(8)$. The physical interpretation of such terms is that there is a finite probability of all eight electrons being piled momentarily on one hydrogen atom, since $\mathrm{I}(j)$ means a hydrogen wave function in which electron j is attached to nucleus a. There are also other terms involving accumulation of from 2 to 7 electrons on the same H atom. Analogous results are found in Hund's calculations for H_2 and H_2O, where respectively 2 and 4 electrons can accumulate on an H atom. Fortunately, all these remarks apply only as long as we take the wave functions to be simple products such as (5) of "one-electron functions." Actually, the seriousness of the accumulation effects is considerably diminished from the foregoing when one includes the spin and "antisymmetricizes" so as to satisfy the Pauli principle. One must, of course, take the antisymmetrical linear combinations, inclusive of spin functions, since the wave function (5) is not unique because of the possibility of permutation of electrons. As long as we have agreed to include electron repulsions only insofar as they can be represented by the self-consistent field, the process of taking such combinations will have no effect upon the energy provided we neglect terms resulting from the want of orthogonality of the wave functions $\mathrm{I}, \mathrm{I}', \cdots, \mathrm{IV}'$ etc., i.e., provided we neglect the elements dW, fW, hW in (2). When linear combinations are taken in accordance with the Pauli principle, it is found that not more than two electrons can accumulate on a given nucleus. In other words, the final wave function will involve terms such as $\mathrm{I}(1)\mathrm{I}(2)\mathrm{II}(3)\cdots$, but none such as $\mathrm{I}(1)\mathrm{I}(2)\mathrm{I}(3)\cdots$. For this observation the writer is indebted to Professor Slater. Similarly in Hund's model of H_2O, only

two electrons can accumulate on one H nucleus when the exclusion principle is taken into account.

To prove that the exclusion principle reduces accumulation as stated above, one utilizes the well-known result of Slater's paper on complex spectra,[11] that the complete wave function, inclusive of spin, can be written as a sum of determinants. The elements of a determinant consist of the product of a spin factor and an orbital wave function. Elements of the same column have the same coordinate and spin arguments, i.e., relate to the same electron, but have different spin or orbital functions, while elements of the same row all involve the same functions but with different arguments. In our case the orbital factors of each element may without loss of generality be considered to be one of the eight expressions $\mathrm{I}\cdots\mathrm{IV}'$, since provision for linear combinations is made when it is stated that the complete wave function is the *sum* of determinants. Because the spin factor can only assume two different values $\delta(-\frac{1}{2};\, m_s)$, $\delta(\frac{1}{2};\, m_s)$, any given one of the expressions $\mathrm{I}\cdots\mathrm{IV}'$ cannot appear in more than two rows of any determinant without the latter vanishing. From this it follows that the expansion of the complete wave function cannot involve terms in which any one of these expressions appears as a factor more than twice, Q.E.D.

Another unpleasant feature is that much of the expansion of (5) represents terms of the structures $C^{4+}(H_4)^{4-}$, $C^{3+}(H_4)^{3-}$, $\cdots$, $C^{4-}(H_4)^{4+}$, even though in the mean the molecule is not ionic. For instance, if $\beta_1^2=\beta_2^2=\frac{1}{2}$ and if we neglect corrections for non-orthogonality, the C and collectively the four H atoms share the 8 electrons equally on the average but one calculates that then the molecule spends the following percentages of the time in various structures: $C^0(H_4)^0$, 27 percent; $C^+(H_4)^-$, 22; $C^-(H_4)^+$, 22; $C^{2+}(H_4)^{2-}$, 11; $C^{2-}(H_4)^{2+}$, 11; $C^{3+}(H_4)^{3-}$, 3; $C^{3-}(H_4)^{3+}$, 3; $C^{4+}(H_4)^{4-}$, $\frac{1}{2}$; $C^{4-}(H_4)^{4+}$, $\frac{1}{2}$. (The process of antisymmetricizing does not affect the percentages of distribution between C and 4H, but does show that in $C^{4+}(H_4)^{4-}$ the 8 electrons are always distributed evenly between the 4 hydrogen nuclei.) This is entirely too much instantaneous polarity. The excessive instantaneous polarity demanded by the Hund-Mulliken method is glaringly revealed in the case of H_2, where this method predicts the molecule to be H^+H^- and H^-H^+ half the time, whereas calculation shows that it probably is so constituted only 1/64 of the time.[12] If the transfer effects are as frequent in CH as in H_2, and if those in CH_4 can be roughly estimated by fourfold superposition of those in CH, then this value 1/64 suggests that methane should be $C^+(H_4)^-$ or $C^-(H_4)^+$ each only 3 percent of the time and be in doubly or more ionic states (all kinds combined) less than 1 percent. The excessive accumulation effects can be eliminated by extending Mulliken's method by adding to (5) other solutions in which one or more electrons settle in the higher[13] roots of the determinants (4). Essentially because the presence of nodes increases materially the normalization constants for the higher states, the amount of such states which must be added to (5) is surprisingly small, at least in H_2, where Mulliken notes[12] that the accumulation effect is properly reduced by adding[14] $\psi_u(1)\psi_u(2)$ to $\psi_g(1)\psi_g(2)$ in the ratio of only 1 to 8. This suggests that it probably would be quite a good approximation if we could make a calculation in which (5) is augmented by linear combination with states in which only one or two electrons settle in the higher roots of (4). Such a calculation, however, presents serious mathematical difficulties, and without it the Hund-Mulliken method must be regarded more as a qualitative rather than quantitative procedure.

The preceding result that two electrons can occasionally accumulate on one atom is, of course, in sharp contrast to the high degree of localization found in the Slater-Pauling model, and related Heitler-London methods of calculation which assign one and only one electron to an H atom. Naturally, accurate inclusion of the electron repulsion prevents accumulation being realized to the extent predicted by the preceding

[11] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[12] See discussion by R. S. Mulliken, Phys. Rev. **41**, 69–71 (1932) based on a calculation by Slater, ibid. **35**, 514–515 (1930).

[13] Do not confuse our references to the higher and lower roots of an individual determinant of (4) with the upper and lower choices of sign which yield the two determinants.

[14] Here, as usual, the notation ψ_g, ψ_u means wave functions respectively even and odd with respect to reflection in the midpoint of the internuclear axis. The corresponding notation in reference 12 is ϕ_0, ϕ_1.

calculation. We have agreed to neglect this repulsion except via the self-consistent field, and under such neglect the question of accumulation is irrevelant for the time being, but any wave functions giving pronounced accumulation will be rather severely perturbed, and hence cannot be regarded a good approximation, if the theory is refined by introducing accurate consideration of the electron repulsions as a perturbation. Strict localization of one electron to an H atom could have been achieved if we had not taken the linear combinations (3) but had instead kept the hybridized sp^3 wave functions and had used only twofold linear combinations of the form $\alpha\mathrm{I}+(1-\alpha^2)^{\frac{1}{2}}\mathrm{I}'$ etc., which, as already stated, represent purely localized bonds. Such a mode of securing localization would involve the error of neglecting the elements b, e, f, g, h in (2) since these elements cannot be brought onto the diagonal by taking such twofold (rather than eightfold) linear combinations. This error we shall call for brevity the neglect of individual symmetry type inasmuch as the wave functions representing sp^3 bonds are thus inadequate to diagonalize (2) or in other words lack the symmetry properties characteristic of irreducible representations of the tetrahedral group. The word "individual" is inserted because the symmetry considerations relate to wave functions of an isolated electron. When electron repulsions are accurately included, the dynamical problem ceases to be that of a one-electron system, and so symmetry properties for individual electrons are no longer preserved. Nevertheless, they will not be seriously impaired if the Hartree self-consistent field has been a good approximation.

The seriousness of neglecting symmetry type is gauged by the magnitude of b, e, f in (2), or more succinctly, by the separation of the lower roots[13] of the two determinants (4) since if these roots coincided their wave functions could be combined by a process more or less the reverse of (3) into those representing localized sp^3 bonds. If the carbon levels are lower than the hydrogen ones, the two lower roots of (4) are $W=a+3b$, $W=a-b$ when $c=d=e=f=0$, as is the case when all interaction between the C and H atoms is neglected. Hence $4b$ has the significance of being the carbon s-p separation, and neglect of individual symmetry type will be a poor approximation if this separation is greater than or comparable with the C−H bonding energy. Actually the s-p interval in carbon amounts to a few volts, and hence is not negligible compared to the energy of a C−H bond (4 volts). (The value of the s-p interval in C depends on which spectral terms are selected from the configurations sp^3 and s^2p^2; the lowest state ^3P of s^2p^2 is 1.6 volts below ^5S of sp^3, according to rather indirect evidence from band spectra,[15] and is definitely known to be from 8 to 10 volts below most[16] other terms ($^1P, ^3P, ^1D, ^3D$) belonging to sp^3. Since a one-electron model is inadequate to take account of different term values for the same configuration, it is perhaps fairest for our purposes to compare the mean of all terms arising from s^2p^2 with the mean of all terms from sp^3. When allowance is made for the fact that the two other terms ^1D, ^1S of s^2p^2 are 1 and 2 volts higher than ^3P, the difference between the two means is found to amount to 6 or 7 volts.) Even if the $s-p$ separation of carbon were zero, the neglect of individual symmetry type would not be a good approximation as the two determinants (4) are not identical even when $b=0$. The situation is thus quite different from that which Hund[6] encounters in a strictly right-angled model of H_2O, where only p wave functions are used for the O valences, and where he shows that the two lower roots of his two determinants exactly coincide, so that the error due to neglect of individual symmetry type in securing localized bonds is nil.

To summarize, the Slater-Pauling localized bonds avoid excessive electronic accumulation on the same atom, but give rather too great departures from individual symmetry type. These properties were, in fact, already known in a very general way, but it seems instructive to us to have deduced them more concretely by means of the secular determinant (2).

In Part II we shall give calculations which aim to show that the tetrahedral model of CH_4 is firmer than other models in both the Hund-Mulliken and Slater-Pauling methods, even without invoking H−H repulsions.

The writer is indebted to Professor R. S. Mulliken for helpful discussion and correspondence.

[15] W. Heitler and G. Herzberg, Zeits. f. Physik 53, 52 (1929).

[16] The location of the remaining term $sp^3\ ^3S$ is unknown.

Effects of Pressure on the Visible Band Spectra of Nitrogen

HERBERT S. HARNED AND EUGENE R. BROWNSCOMBE,* *Department of Chemistry, Yale University*

(Received January 7, 1933)

(1) The visible band spectrum of nitrogen produced by an electrodeless discharge has been studied at pressures ranging from 0.002 to 4 mm. (2) At the lowest pressures the spectrum was almost entirely composed of the first negative bands due to N_2^+. The first positive bands appeared very faintly. As the pressure of the discharge was increased, the first and second positive band systems greatly increased in intensity up to a pressure of 0.2 mm. At still higher pressures the second positive bands were found to fade until at pressures of 4 mm they were just noticeable. (3) In the case of the first negative bands, it is found that increase of pressure increases the number of N_2^+ ions in the higher rotational states.

EXPERIMENTAL

THE spectra were excited by means of an electrodeless discharge. A high-frequency oscillation was maintained in a copper helix in the center of which was the discharge tube. The oscillator circuit was similar to that recently described by Hunt and Schumb.[1] The exciting coil was made of 1/8″ copper tubing wound in a helix 4″ in diameter, the turns being 1/2″ apart. A 50-watt oscillator (De Forest Type 503A) was used. When adjustments were made, the plate current was 60 m.a. when there was no discharge in the tube. This was convenient because when the glow in the discharge tube was highest the plate current rose to 100 m.a.

The wave-length of the oscillator was 16 meters (19×10^6 cycles). There is every reason to believe that the excitation was electrostatic rather than electromagnetic.[2] The oscillator produced a continuous wave, so that the rate of change of magnetic flux was small. Uniform glow was obtained throughout the tube, and no indication of ring discharge was noticeable. The pressure range over which the discharge could be obtained was very considerable. From 20 mm down to the lowest pressures obtainable with diffusion pumps and a liquid air trap, certainly less than 10^{-6} mm, light glows were obtained. At the lowest pressures, the gray glow formed when the discharge was turned on, disappeared in a few seconds and gave way to brilliant variegated colors on the inner surface of the tube.

The discharge tube was of quartz and was 12″ long and 3/4″ in diameter. A quartz optical window was fused on an end. A quartz tube is very desirable even when working with visible spectra since it can be heated in vacuo to high temperatures to remove adsorbed impurities. It was connected to the rest of the apparatus by a quartz to Pyrex seal. A liquid-air trap was inserted between the tube and the rest of the apparatus which served to keep mercury from the diffusion pumps and other impurities from the tube. The gas was admitted to the tube through this trap.

A large Universal Schmidt and Haensch Spectrograph was employed. For visible regions the optical system contained two Rutherford prisms, dispersion (C−F 6° 52′). The slit mechanism of the spectroscope was placed close to the quartz window of the tube without an intervening lens.

Tank nitrogen was used in most of the observations. This was found justifiable since the spectrum obtained was identical with that obtained by nitrogen prepared by heating potassium nitrite. Spectra were obtained at pressures of 0.002, 0.007, 0.013, 0.025, 0.05, 0.13, 0.2, 0.4,

* The material contained in this contribution constituted part of a dissertation presented by Eugene R. Brownscombe to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

[1] Hunt and Schumb, J. Am. Chem. Soc. **52**, 3152 (1930).

[2] MacKinnon, Phil. Mag. **8**, 605 (1909); Brasfield, Phys. Rev. **35**, 1073 (1930); Lynch and Hilberry, ibid. **37**, 1091 (1931); Knipp and Knipp, ibid. **38**, 948 (1931).

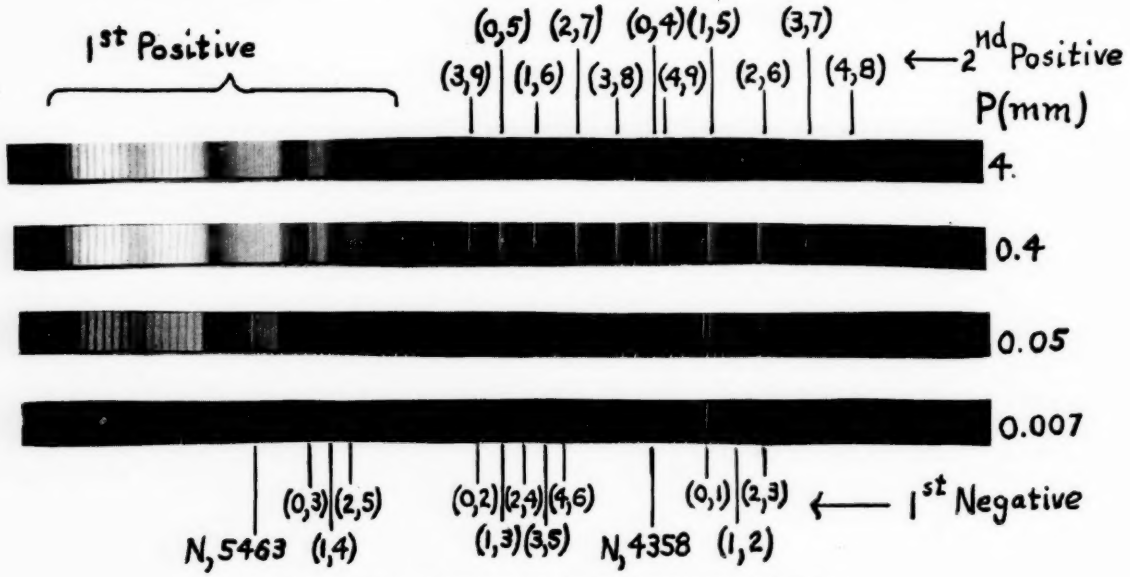

FIG. 1. Effect of pressure on the band spectrum of nitrogen.

0.8, 2.2 and 4 mm. Five-minute exposures were used.

RESULTS AND DISCUSSION

The effects of pressure on the entire visible band spectrum are illustrated by Fig. 1, in which photographs obtained at the pressures indicated at the right are shown.[3] At the lowest pressure, every line observable at wave-lengths less than 5500A is due to the spectrum of the first negative group due to N_2^+ with the exception of the two lines of atomic nitrogen indicated at 5463A and 4358A. The vibration-band heads of this system of bands are indicated and designated by the vibrational quantum numbers given at the bottom of the illustration. At the red end, the first positive group of bands due to neutral nitrogen appear faintly. As the pressure is increased, the first positive group increases greatly in intensity, and there also appears at pressures above 0.01 mm another band system due to neutral nitrogen and designated the second positive group. The vibration-band heads of the second positive group are marked and designated by their vibrational quantum numbers at the top of the illustration. Upon closer observation it is interesting to note that the intensity of the second positive group increases up to a pressure of 0.2 mm and then decreases with further increase in pressure until at a pressure of 4 mm it is just noticeable. This particular point is more clearly indicated in Fig. 2 in which an enlargement of that part of the spectrum in Fig. 1 which includes the (0, 1) and (1, 2) bands of the first

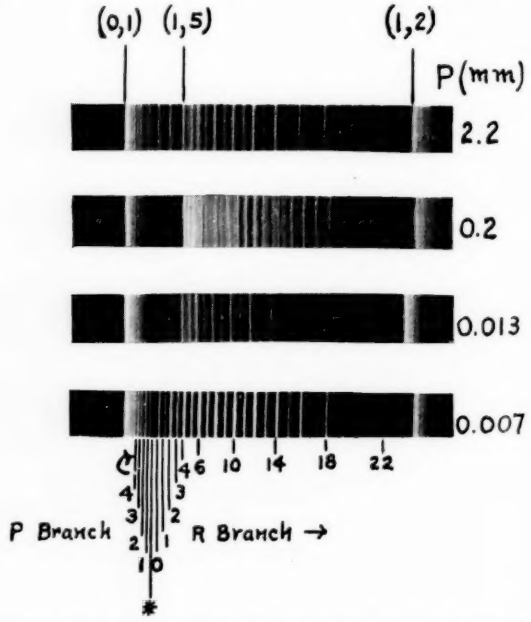

FIG. 2. The (0, 1) and (1, 2) first negative bands and the (1, 5) band of the second positive.

[3] For a general discussion of these band systems, see Weizel, *Bandenspektren*, pp. 346–361, Handbuch der experimental Physik, Erganzungswerk, Band 1, Akad. Verlagsgesellschaft, Leipzig, 1931.

negative group and the (1, 5) band of the second positive group is shown.

In discharges of this kind, it is to be expected that the negative bands or atomic lines persist at all pressures, since the presence of both positive ions and electrons are necessary in order for the discharge to persist. In similar experiments with oxygen, the second negative bands due to O_2^+ were found to be intense over a large pressure range. In the case of hydrogen, it is well known that no spectrum due to H_2^+ appears, but in this case the atomic lines are very intense at all pressures as are those due to the band spectrum of H_2. Thus, the presence of bands due to N_2^+ is to be expected. Further, an activated neutral molecule can result from a three-body collision between a positive ion, a molecule and an electron, so that at the higher pressures we may expect the appearance of the positive groups of bands. The fact that the second positive group decreases in intensity at the higher pressures shows that the energy exchanges bear a complicated relation to the number of collisions. Under the conditions of these experiments, the energy contributed to the gas in producing the discharge was nearly the same at all pressures. Similar results were obtained in the region of the (0, 0) band of N^{2+} at 3195A.

The structure of the first negative bands has been studied by Fassbender[4] and Herzberg[4] and is of the $^2\Sigma - {}^2\Sigma$ type. The rotation structure possesses a P and an R branch but no Q branch. The well-known phenomenon of alternating intensities in these lines appears very clearly. Measurements of the lines of the N_2^+ bands from the plates obtained at 0.007 mm and 4 mm were made and were found to agree within ± 0.1 of a wave number. These measurements with vacuum correction also agreed within the same limits with the values given by Fassbender. The equations for the two branches,

$$P(K) = 23391.01 - 3.99K + 0.19K^2$$

and

$$P(R) = 23391.01 + 3.99(K+1) + 0.19(K+1)^2,$$

were found to represent the measurements to within ± 0.05 of a wave number. From this, the moments of inertia of the lower and higher vibrational states were found to be

$$I' = (13.23 \pm 0.05) \times 10^{-40}\ \text{g}\cdot\text{cm}^2$$

and

$$I'' = (14.56 \pm 0.05) \times 10^{-40}\ \text{g}\cdot\text{cm}^2.$$

13.35 and 14.41 have been given for I' and I'' of the (0, 0) band.[5] The origin of the band and some of the rotational quantum numbers of the P and R branches are indicated at the bottom of Fig. 2. The structure of the second positive band is a $^3\Pi - {}^3\Pi$ type.[6] No attempt was made to measure the lines of this band. One further fact was observed from microphotometer traces obtained at the higher and lower pressures. At higher pressures, the intensity of the lines at higher quantum numbers was relatively greater than their intensities at lower pressure. This is illustrated clearly in Fig. 3 where the intensities, roughly determined from the microphotometer traces, are plotted against the rotational quantum numbers, in this case the even numbers, at pressures of 0.007 and 2.2 mm. The odd-numbered lines show an exactly similar behavior. Since between the quantum numbers 4 and 10 the N_2^+ lines are augmented in intensity by the lines of the second positive band, it is roughly estimated that the distribution of intensities is more truly represented by the solid line than by the dotted one given by the measurement. There seems to be little doubt that pressure increases the number of N_2^+ ions in the higher rotational quantum states.

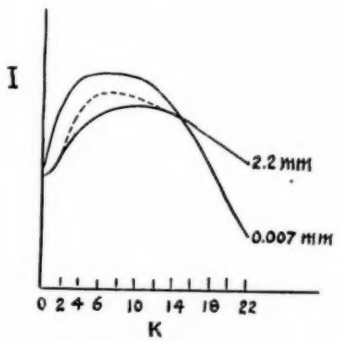

FIG. 3. Intensities of the lines of (0, 1) first negative band of nitrogen.

[4] Fassbender, Zeits. f. Physik **30**, 73 (1924); Herzberg, Ann. d. Physik **86**, 189 (1928).

[5] International Critical Tables **5**, 415 (1929). McGraw-Hill Book Company.

[6] Lindau, Zeits. f. Physik **25**, 247 (1924); **26**, 343 (1924); **30**, 187 (1924).

The Exchange of Energy Between Polyatomic Molecules and a Metallic Surface

FRED R. WHALEY,* *Department of Chemistry, Johns Hopkins University*

(Received January 13, 1933)

Experimental evidence is given to show that fairly complicated molecules, on striking a hot surface, do not absorb energy in their vibrational degrees of freedom to any appreciable extent. In regard to the energy interchange the molecules behave like hypothetical gases of six degrees of freedom, translational and rotational.

MOST of the work reported on energy exchanges between gases and solids deals with light monatomic or diatomic molecules. However, Rice and Byck[1] in attempting to decompose acetone and dimethyl mercury by impinging it on a platinum surface at 1600°C concluded that the "transfer of energy from a heated target to the internal degrees of freedom of an organic molecule is not 100 percent efficient." The purpose of this work is to show experimentally that, when fairly complicated molecules strike a hot surface, the efficiency of energy transfer from the solid surface to the vibrational degrees of freedom of the impinging molecule is very low and, within the limits of experimental error, possibly equal to zero.

The apparatus consisted essentially of a water-cooled, cylindrical chamber about 10 cm long and 4 cm in diameter, in which was suspended a platinum wire. With the aid of tungsten leads sealed through the glass, the wire could be heated electrically and its temperature calculated from its resistance. Allowance was made for the almost negligible resistance of the leads, and this correction was kept constant by keeping the leads at the temperature of solid CO_2 throughout all the readings. A bulb containing the substance being used and surrounded by a bath of alcohol and solid CO_2, was connected with the chamber. The pressure in the chamber could be measured by means of a McLeod gauge, so constructed that when pressure measurements were taken the pressure of the vapor in the capillary was only a fraction of the vapor pressure at room temperature of the substance used. The chamber could be evacuated either rapidly through a wide tube or slowly through a capillary.

A calibration curve was obtained by evacuating the chamber to about 10^{-4} mm of Hg and plotting the energy input in the wire against the temperature of the wire. Due to varying conditions of the surface of the chamber, probably because of platinum and carbon deposited there, the calibration curves varied slightly from day to day. Curves obtained before and after a run agreed, however, so separate calibration curves were made with each run.

The run itself was made by keeping the substance in the chamber at a known pressure and again plotting energy input against temperature. At a given temperature the energy given up to the colliding molecules could at once be read from the graph. This was compared with the energy exchange calculated, assuming the gas to be a hypothetical gas of only six degrees of freedom, translational and rotational.

In this calculation the following equation derived by Langmuir[2] was used:

$$m = p(M/2\pi RT)^{\frac{1}{2}},$$

where m = grams striking surface per second per cm^2; p = pressure; M = molecular weight; T = absolute temperature; R = gas constant. The mols per second hitting wire $= mA/M$ where A is the area of the wire. The energy absorbed per second in watts is:

$$[4.185mA(T_2 - T_1)C_v]/M,$$

where $(T_2 - T_1)$ is temperature difference between wire and walls and C_v is the specific heat.

* Du Pont Fellow.

[1] F. O. Rice and H. Byck, Proc. Roy. Soc. **A132**, 50 (1931).

[2] I. Langmuir, Phys. Rev. **2**, 329 (1913).

Runs were made with chloroform, acetone, methyl alcohol, carbon tetrachloride and ethyl acetate. The substance was kept at constant pressure during a run by the constant-temperature bath and the slow pumping through the capillary. The pressure should be sufficiently low that the temperature distribution of the molecules colliding with the wire is equal to the distribution of molecules in temperature equilibrium with the walls. This means that the mean free path must be at least as great as the diameter of the wire, and preferably two or three times as great.

In the runs with methyl alcohol, carbon tetrachloride and ethyl acetate the pressure was sufficiently low, the highest being 0.047 mm for ethyl acetate. The mean free path was 0.034 cm. The diameter of the wire was 0.025 cm.

Let us designate the molecules about to strike the wire as A molecules. These had their last collision with other molecules, which we shall call B molecules, when they were at an average distance from the wire equal to Λ, the mean free path. The A molecules will have a temperature distribution equal to that of the main body of the gas, unless an appreciable fraction of the B molecules just came from the wire, hence having a temperature increment. That fraction is approximately the angle in radians subtended by the wire from a point at distance Λ, divided by 2π.

In the ethyl-acetate run this fraction is about 0.12, but the A molecules, colliding with B molecules coming from the wire, can at best receive a temperature increment of half the increment received by the B molecules. Since the efficiency of energy transfer on collision may not be perfect, the error due to this preheating of the A molecules is probably even less than the maximum error, which is $0.12/2=0.06$ or 6 percent. This is within the limits of experimental error. For methyl alcohol and carbon tetrachloride the error is even less. Figs. 3, 4 and 5 show the marked agreement between the observed energy changes and those calculated for a hypothetical gas of six degrees of freedom.

In the chloroform and acetone runs this error is about 13 percent, which is too high even allowing for inefficient energy exchanges between molecules A and B. This would tend to make the calculated energy exchange too high. Figs. 1 and 2 show a calculated value higher than the measured value.

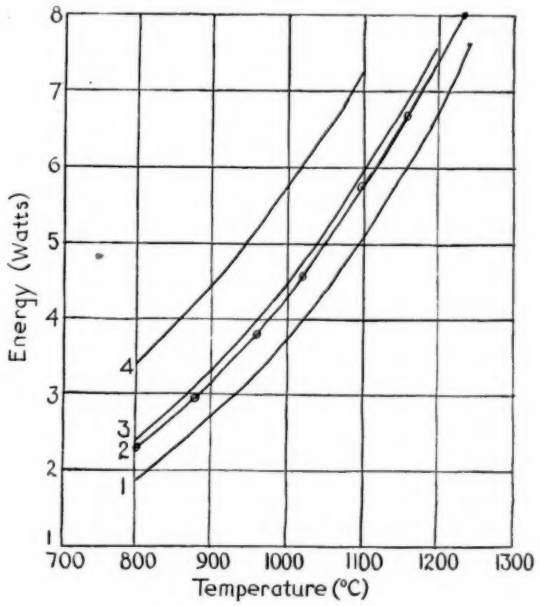

FIG. 1. Chloroform.

In each graph, 1 is the calibration curve, 2 is the observed energy curve and 3 is the energy curve calculated on the basis of perfect efficiency in energy transfer to translational and rotational

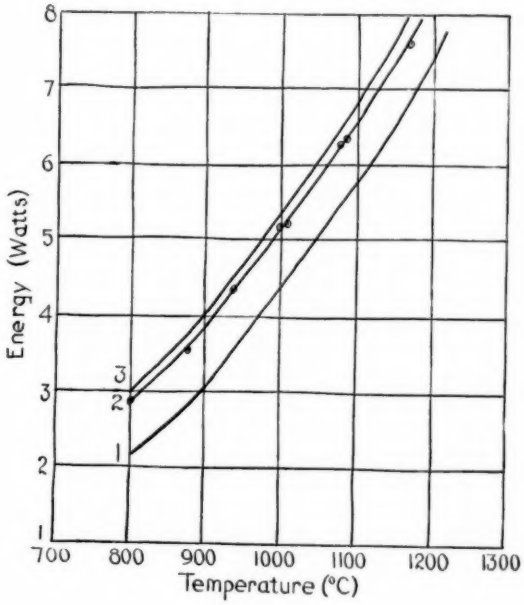

FIG. 2. Acetone.

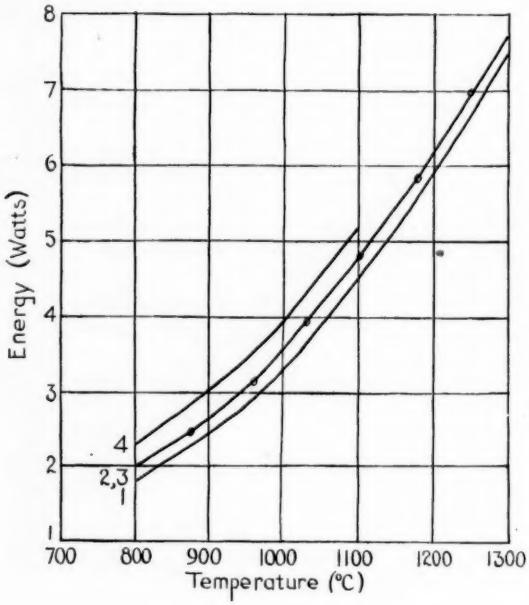

FIG. 3. Methyl alcohol.

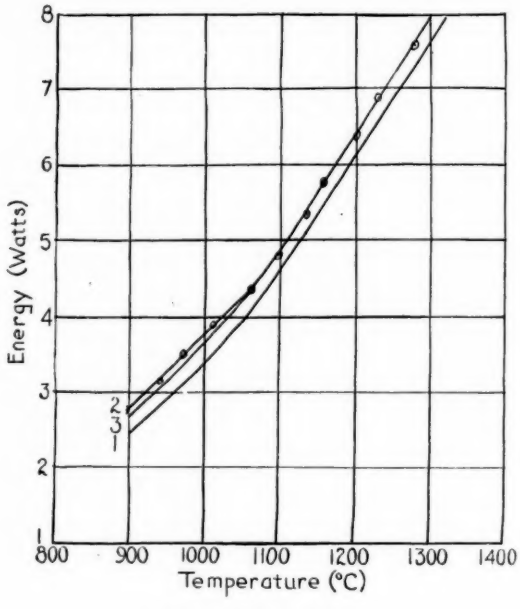

FIG. 5. Ethyl acetate.

degrees of freedom and no transfer of energy to the vibrational degrees of freedom. Curve 4 is calculated by assuming perfect efficiency of energy transfer to all degrees of freedom. (Specific heat values were calculated by Dr. D. H. Andrews and his students in this laboratory from Raman data.) Experimental points on curve 2 are shown. Table I summarizes the conditions under which the experiments were carried out for each of the substances studied.

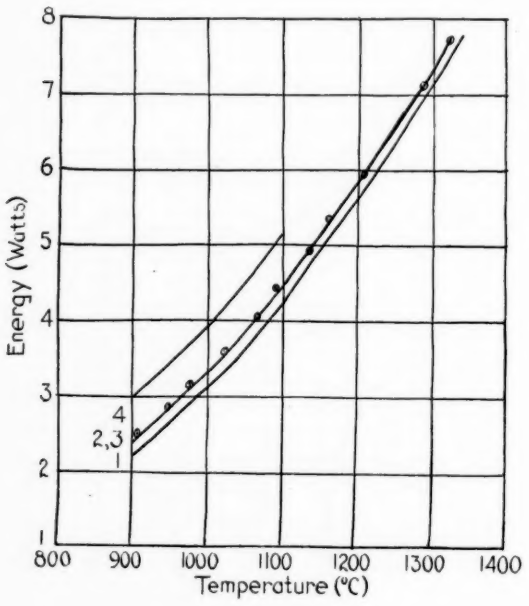

FIG. 4. Carbon tetrachloride.

TABLE I.

Substance	Pressure (mm)	Λ at 0°C and one atm. (cm)	Λ at press. used (cm)	Ratio of Λ to wire diam.
$CHCl_3$	0.140	265×10^{-8}	0.014	0.56
CH_3COCH_3	0.146	258×10^{-8}	0.013	0.52
CH_3OH	0.0256	517×10^{-8}	0.153	6.10
CCl_4	0.0376	326×10^{-8}	0.066	2.64
$CH_3COOC_2H_5$	0.047	212×10^{-8}	0.034	1.36

DISCUSSION

Zener[3] concludes from theoretical considerations that light molecules of light atoms colliding with each other exchange rotational quantum numbers freely, but that the transfer of vibrational energy may be difficult even in cases of exact resonance. Although in the work reported here one of the colliding bodies is platinum and not a "light molecule," the results seem to conform with Zener's conclusion.

[3] C. Zener, Phys. Rev. 37, 556 (1931).

Herzfeld and Göppert Mayer[4] showed from theoretical considerations that the time necessary for an organic molecule, adsorbed on a hot surface, to absorb energy in its vibrational degrees of freedom was longer than the collision time. The results reported here are in accord with that theory.

Van Wijk[5] by optical methods shows that the accommodation coefficient for rotational energy in the case of H_2 is very small. Knudsen[6] by measuring radiometer pressures finds that the accommodation coefficient for the internal energy of H_2 can be equated to the accommodation coefficient for the translatory energy. The work of both these authors with H_2 seems to be contrary to the results reported here, but the latter deal with heavier and more complicated molecules.

The author wishes to express his sincere appreciation to Professors D. H. Andrews and K. F. Herzfeld and Dr. J. E. Mayer for their kind suggestions and advice during the carrying out of this research.

[4] Herzfeld and Göppert Mayer, Zeits. f. physik. Chemie Bodenstein Festband, 669 (1931).

[5] Van Wijk, Zeits. f. Physik **75**, 584 (1932).

[6] M. Knudsen, Ann. d. Physik **6**, 129 (1930).

Induction Between Bond Moments in Some Halogenated Methanes

C. P. SMYTH AND K. B. MCALPINE, *Princeton University*

(Received December 16, 1932)

The dipole moments of four fluorochloromethanes are measured in the vapor state. The inductive effects of carbon-halogen bond moments are calculated and, through these, the moments of methyl fluoride and methyl chloride are used to calculate approximate values for CH_2Cl_2, $CHCl_3$, and $CFCl_3$, which are in satisfactory agreement with the observed values. The moments of these molecules are then used to calculate values for other substituted methanes which are in excellent agreement with the observed values. The value of a bond moment is treated as a function of its environment.

IN an earlier paper[1] experimental determinations of the dipole moments of di- and tribromo- and iodomethanes were reported and the results were confirmed by the measurements of Müller and Sack.[2] In this first paper on the substituted methanes the moment of each molecule was treated as the resultant of the moments of dipoles lying in the lines joining the carbon and halogen nuclei. The observed moments were smaller than those calculated on the assumption that these bond moments did not affect one another and acted at an angle of 109.5° to one another, the normal carbon tetrahedral valence angle. Kinetic theory diameters were, therefore, calculated for the halogen atoms and assumed to cause widening of the valence angles, which were calculated from these diameters and from the carbon-halogen nuclear separations estimated from spectroscopic and x-ray data. The distance between the two chlorine nuclei in methylene chloride was calculated to be 3.00A, while Wierl[3] later found from electron diffraction a distance of 3.16 ± 0.06A in methylene chloride and 3.04 ± 0.04A in chloroform. In methylene bromide, the distance between the bromine nuclei was calculated to be 3.20A, while Wierl found 3.35 ± 0.04A in carbon tetrabromide, and, in methylene iodide, the distance between the iodine nuclei was calculated to be 3.62A, while Huggins and Noble,[4] by means of x-ray analysis, found 3.56A in crystalline iodoform and reported values 3.86 and 3.80 ± 0.2A as found by Brockway and Pauling for iodoform in benzene solution. The angles between 120° and 135° obtained from these calculated distances gave calculated dipole moments in excellent agreement with the observed, an agreement which was termed somewhat fortuitous because of the speculative nature of the reasoning, uncertainties in some moment values, and neglect of the inductive effect of each dipole upon the rest of the molecule.

Smallwood and Herzfeld[5] showed that this inductive effect could lower the moment of an ortho-disubstituted benzene from the value calculated as the resultant of two mutually independent dipoles acting at an angle of 60° to each other to the observed value, a not inconsiderable decrease. As the dipoles in the halogenated methanes are closer together than those in the ortho-disubstituted benzenes, it is evident that some attempt should be made to take account of their inductive effects.

Wierl's electron diffraction experiments give larger carbon-halogen distances than do Pauling's atomic radii[6] and valence angles between 110° and 115° for the chlorinated methanes, not establishing the existence of any widening of the valence angle beyond the regular tetrahedral angle rounded off to 110°. In view of this, we shall examine the moments of chlorine-substituted methanes with 110° valence angles assumed between the bonds and shall tentatively make a

[1] C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930).

[2] H. Müller and H. Sack, Phys. Zeits. **31**, 815 (1930).

[3] R. Wierl, Ann. d. Physik [5] **8**, 521 (1931).

[4] M. L. Huggins and B. A. Noble, Am. Mineral. **16**, 519 (1931).

[5] H. M. Smallwood and K. F. Herzfeld, J. Am. Chem. Soc. **52**, 1919 (1930).

[6] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

similar assumption in the case of fluorine-substituted methanes, although calculation shows the possibility of a greater widening of the angle between two C—F bonds than that in the case of two C—Cl bonds.

The kindness of Dr. Albert L. Henne of Ohio State University has made it possible for us to measure four pure samples of methanes containing both fluorine and chlorine substituents prepared by him.

Experimental Results

The dielectric constants ϵ of the four vapors were measured with an apparatus and method described elsewhere. From each measurement of the dielectric constant, the polarization was

Table I. *Experimental data.*

$CHFCl_2$			CHF_2Cl			$CFCl_3$			CF_2Cl_2		
T(°K)	p(mm)	P	T(°K)	p(mm)	P	T(°K)	p(mm)	P	T(°K)	p(mm)	P
304.7	426.3	51.36	303.9	971.5	55.95	299.2	586.6	29.00	304.7	738.7	25.93
	313.5	51.01		748.2	55.69		577.5	29.16		515.4	25.70
	246.0	50.85		579.4	55.50		541.3	29.23		471.0	25.58
	244.3	50.96		413.9	55.30		518.3	28.97		465.4	25.58
	227.6	50.83		273.0	55.06		424.4	28.71		459.8	25.76
	0	50.55		228.8	54.86		293.7	28.61		435.7	25.75
				157.7	54.73		261.6	28.62		354.4	25.60
305.8	388.6	51.12		0	54.75		250.2	28.49		162.3	25.76
	335.1	50.97					0	28.06		0	25.35
	329.4	50.98	311.0	679.5	54.69						
	283.4	50.92		674.3	54.66	304.3	499.5	28.69	311.1	730.0	25.68
	267.5	50.74		672.7	54.70		490.3	28.70		620.9	25.62
	231.2	51.00		467.4	54.46		436.6	28.72		520.9	25.59
	157.5	50.72		283.0	54.27		359.0	28.58		385.4	25.40
	0	50.55		219.6	53.90		277.3	28.27		0	25.20
				0	53.82		182.6	28.22			
340.0	467.5	47.63					180.7	28.20	348.8	680.6	24.94
	358.3	47.55	347.9	659.8	50.24		0	27.92		529.4	24.87
	344.1	47.45		526.6	50.05					509.1	24.80
	319.7	47.64		447.2	50.14	322.6	565.8	28.48		385.3	24.82
	247.0	47.16		283.1	49.69		545.3	28.46		325.1	24.80
	212.8	47.35		0	49.65		515.9	28.35		251.3	24.43
	184.1	46.80					515.7	28.42		0	24.67
	0	47.10	391.5	706.4	46.18		422.3	28.38			
				586.8	46.14		369.6	28.22	389.2	917.7	24.33
385.3	590.8	44.34		451.6	46.13		347.2	28.28		763.4	24.25
	494.4	44.18		400.7	45.91		290.5	28.12		633.5	24.34
	403.1	44.05		223.4	45.70		279.8	28.35		573.3	24.27
	382.5	44.08		0	45.80		272.9	28.19		413.2	24.19
	338.6	44.11					0	27.88		0	24.28
	329.1	44.08	433.0	760.0	43.23						
	295.8	44.00		602.9	43.17	342.6	529.1	28.08	421.2	914.6	23.98
	0	43.70		591.1	42.97		510.8	28.04		900.5	23.91
				532.4	42.99		456.0	27.95		780.1	23.86
424.3	639.6	41.95		469.4	43.28		366.1	27.82		722.5	23.89
	519.6	41.85		446.7	42.82		269.7	27.73		619.7	23.92
	474.1	41.74		0	42.80		261.6	27.72		0	23.91
	371.3	41.43					193.5	27.25			
	357.9	41.57	478.7	721.6	40.19		189.9	27.40	470.3	959.7	23.59
	0	41.14		651.0	40.30		186.9	27.44		926.2	23.67
				612.5	40.16		182.9	27.01		920.3	23.45
				546.9	40.49		0	27.40		848.4	23.56
				455.5	40.18					787.8	23.39
				446.9	40.25	375.9	568.2	27.61		785.8	23.39
				0	40.25		541.0	27.66		0	23.51
							455.6	27.56			
							360.6	27.48			
							350.7	27.78			
							264.9	27.45			
							257.4	27.53			
							256.8	27.27			
							0	27.23			

calculated as

$$P=[(\epsilon-1)/(\epsilon+2)]V, \qquad (1)$$

where V is the molar volume. As the ideal gas law was used in calculating P, the dielectric constant was measured for several different pressures at each temperature and the calculated polarizations were extrapolated to zero pressure to obtain a value of the polarization free from error caused by deviations from the ideal gas law. It may easily be shown that, at these pressures, the polarization-pressure curve is practically a straight line with a slope proportional to the second virial coefficient of the gas. Extrapolation of the polarization to zero pressure is, therefore, a simple matter, although the accuracy of the polarization values is insufficient to give a satisfactory value for the second virial coefficient.

Table I gives the values of the polarization for the different pressures at each temperature on the absolute scale, the extrapolated values being given for zero pressure. These latter values were used to calculate for each substance the constants of the Debye equation,

$$P=a+b/T. \qquad (2)$$

The value of the atomic polarization was calculated as $P_A=a-P_E$, the molar refraction for infinite wave-length, P_E, being obtained by extrapolation from the sums of atomic refractions or of electron group refractions for the sodium D line.[7] The dipole moments were calculated from the values of b as $\mu=0.01273\times10^{-18}(b^{\frac{1}{2}})$ and should be in error by no more than 0.01×10^{-18}. The values of these constants are given in Table II, while Table III lists the moments together with those of other molecules needed for the discussion of the results.

TABLE II. *Constants of substituted methanes.*

	a	P_E	P_A	b	$\times10^{18}$
$CHFCl_2$	17.0	16.1	0.9	10,260	1.29
CHF_2Cl	15.1	11.2	3.9	12,040	1.39_6
$CFCl_3$	23.8	20.8	3.0	1,256	0.45
CF_2Cl_2	20.1	16.0	4.1	1,600	0.51

TABLE III. *Moments* ($\times10^{18}$) *of substituted methanes.*

CH_3F[a]	1.80_8	CCl_4	0[b]	CH_3Cl	1.85[b]
$CHFCl_2$	1.29	CF_2Cl_2	0.51	CH_2Cl_2	1.57[c]
CHF_2Cl	1.39_6	$CFCl_3$	0.45	$CHCl_3$	1.05[b]

[a] Measurement in this laboratory to be published shortly.

[b] Smyth, *Dielectric Constant and Molecular Structure*, Appendix I, New York, The Chemical Catalog Co. Inc., 1931.

[c] K. L. Wolf and O. Fuchs, *Stereochemie* (K. Freudenberg), p. 244, Leipzig, Franz Deuticke, 1932.

Discussion of Results

In view of the very small difference, 0.04 $\times10^{-18}$, between the moment of methyl fluoride and that of methyl chloride, the not inconsiderable moments of CF_2Cl_2 and $CFCl_3$ and the marked increase in moment caused by replacement of chlorine in $CHCl_3$ by fluorine show that the effects of induction and of the widening of valence angles by repulsion must be considered. The zero moments recently reported by van Arkel and Snoek[8] for the moments of $CFBr_3$ and CCl_3Br in benzene solution may be attributed to the fact that moments as small as these should be cannot be accurately determined by measurements on liquids.[9] Although it was possible to explain the moments of CH_2Cl_2 and $CHCl_3$ as the resultants of moments in the C−Cl bonds, the angles between which were widened beyond 110° by mutual repulsion of the chlorines, an analogous explanation of the fluorochloromethane moments is possible only if the fluorine atoms give rise to a much smaller mutual repulsion than that between the chlorines. As a rough calculation of the internuclear distances in methylene fluoride carried out in the same way as those for the other methylene halides indicated a greater repulsion than in the case of the chloride, it would appear that the explanation is to be sought primarily in the inductive effects. This is in accord with the approach to the problem announced at the beginning of the paper because of the closeness of the valence angles of the chloromethanes to 110° found by Wierl and

[7] Landolt-Börnstein, 5th edition, p. 985. Smyth, *Dielectric Constant and Molecular Structure*, p. 153, New York, The Chemical Catalog Co. Inc., 1931.

[8] A. E. van Arkel and J. L. Snoek, Zeits. f. physik. Chemie [B] 18, 159 (1932).

[9] Smyth, *Dielectric Constant and Molecular Structure*, p. 168, New York, The Chemical Catalog Co. Inc., 1931.

because of the considerable inductive effects calculated by Smallwood and Herzfeld for the ortho-disubstituted benzenes.

The polarizability α of a portion of a molecule may, as a rough approximation, be treated as if the polarization occurred at one point. The moment induced at this point by a permanent moment m elsewhere in the molecule can then be calculated by the method of Smallwood and Herzfeld. If the dipole m exerting the force E is located at the origin of a set of plane polar coordinates, the horizontal and vertical components of E(E_x and E_y) at the point r, where the polarizability acts, are given by

$$E_x = m_x(3\cos^2\theta - 1)/r^3 + 3m_y(\sin\theta\cos\theta)/r^3$$
$$E_y = 3m_x(\sin\theta\cos\theta)/r^3 + m_y(3\sin^2\theta - 1)/r^3 \quad (3)$$

where m_x and m_y are the components of m, which lies in the x, y plane. The moment induced by m at the point r has the components

$$m_{ix} = E_x\alpha \quad \text{and} \quad m_{iy} = E_y\alpha. \quad (4)$$

The treatment of the effect of a system of charges as being that of a single dipole located at a point within the system becomes an extremely rough approximation when the effect is considered at distances as small as those involved in the halogenated methanes. Although it is certainly justifiable to treat the principal dipole of CH_3Cl as lying in the C−Cl line, its size and its location in this line are uncertain. In the case of the dihalogenated benzenes, Smallwood and Herzfeld found it necessary to locate the dipoles arbitrarily at the circumference of the carbon atoms to which the particular groups were attached. Consideration of the locations of the centers of gravity of the charges assignable to the C−Cl portion of the molecule places the principal dipole 7/8 of the distance, 1.76A,[6] from the carbon nucleus to the chlorine nucleus.[10] A moment m located at this point would induce a moment in each of the three C−H bonds, which is calculated in terms of m by using Eqs. (3) and (4), the arbitrary assumption being made that a polarizability, $\alpha = 0.66\times10^{-24}$,[5, 11] acts at the midpoint of the C−H bond, 0.53A from the carbon nucleus. If the presumably small and unknown moment of the C−H bond is neglected, the observed moment, 1.85×10^{-18}, may be regarded as the sum of m and the components of the three induced C−H moments along the projection of the Cl−C line. m is thus calculated as 1.15×10^{-18} and the moment induced by it in each C−H as 0.70×10^{-18}. This value 1.15×10^{-18} is, however, too high for the permanent moment of the C−Cl bond as no account has been taken of the inductive effect of the C−H moments, 0.70×10^{-18}, back upon the C−Cl. This effect may be calculated and a still smaller value may be used for the C−Cl moment, the moments induced in the C−H bonds being taken into account in all subsequent calculations. However, in view of our ignorance of the moment of the C−H bond arising from possible inherent electrical unsymmetry and of other uncertainties which cannot be eliminated from the treatment, it appears rational, in cases where at least one hydrogen is attached to the carbon, to assign the entire moment of the methyl halide to the carbon-halogen bond. The results of such treatment will not differ greatly from those to be obtained by using a smaller carbon-halogen bond moment and adding the effects of the C−H bonds.

In the methylene chloride molecule two moments of 1.85×10^{-18} each in the C−Cl lines at an angle of 110° to one another would have a resultant, 2.13×10^{-18}, as compared to the observed value, 1.57×10^{-18}. With the dipoles located 7/8 of the distance from the carbon to the chlorine nucleus, that is, 1.54A from the carbon nucleus, and polarizabilities, $\alpha = 2.51\times10^{-24}$,[5, 11] assumed to be acting at the same points,—a reasonable assumption,—application of our equations shows that the inductive effect of one moment of 1.85 lowers the moment in the other C−Cl line to 1.36. The resultant of two such moments happens to be identical with the observed moment of methylene chloride. However, the moment of 1.36 would have a smaller inductive effect and the lowering calculated for the other C−Cl moment would not be as great. This, in turn, would have a smaller inductive effect upon the first moment. Successive calculations lead to a value 1.49 for the moment of a C−Cl bond when a second chlorine is attached to the same carbon. This would give a moment of

[10] Cf. L. Meyer, Zeits. f. physik. Chemie [B] 8, 27 (1930).
[11] Smyth, Phil. Mag. 50, 361 (1925).

1.71 for methylene chloride if the two C−Cl moments acted at an angle of 110° to each other, but the induced moments do not lie in the C−Cl lines, so that the resultant C−Cl moments make a slightly smaller angle with each other and have a resultant of 1.79, which is 0.22 higher than the observed value for methylene chloride.

Since one C−Cl dipole lowers the moment of another from 1.85 to 1.49, one might, as a very rough approximation, assume that two C−Cl dipoles would produce a lowering of 2×0.36 in a third C−Cl moment. In chloroform, which has a moment $=3(C-Cl)\cos 70°=(C-Cl)$, the moment would, therefore, be 1.13 as compared to an observed value, 1.05. A more accurate treatment involving the calculation of the components along three reference axes leads to a value of approximately 1.35. Obviously, if the assumed location of the permanent dipole is moved in toward the carbon nucleus, the inductive effect will be increased. Thus, with the dipoles and the polarizabilities located 2/3 of the distance from the carbon to the chlorine nucleus instead of 7/8, still much farther from the carbon than assumed by Smallwood and Herzfeld, a C−Cl moment of 1.85 reduces the other C−Cl to 1.03 instead of 1.36 as in the previous case. Although better agreement between the calculated and the observed values of the moments would result from this moving in of the dipoles, such agreement would not be justified by the nature of the treatment. It, therefore, seems better to adhere to the original assumption as to the dipole location, an assumption which is theoretically plausible. Similar calculations show that because of its much smaller polarizability, $\alpha=0.626\times10^{-24}$, the C−F moment is less reduced by the inductive effect of an adjacent C−Cl than is a C−Cl moment, and because of the smaller C−F distance, 1.41A, the C−F moment reduces an adjacent C−Cl moment more than another C−Cl moment does. Table IV gives the lowering of one carbon-halogen bond moment by the inductive effect of another on the same carbon.

The reason for the not inconsiderable moment of $CFCl_3$ is apparent in the marked differences in the moment lowerings in Table IV. The components in the F−C line of the moments induced by the C−F in the three C−Cl's are so large as to cancel a large fraction of the components of the permanent moments in this line, while the C−F moment is less affected by the three C−Cl's. The resultant difference calculated, 1.2, is much larger than the observed moment, 0.45. It is probable that the methyl halide moments assigned to the carbon-halogen bonds include so much of the H−C bond moment, at least, part induced, and, perhaps, part permanent, that they are considerably too high for use when no hydrogen is attached to the carbon. The calculation of the moments induced in the H−C's in methyl chloride gave a moment of 1.15 for the C−Cl and a similar calculation for methyl fluoride gives 0.91 for the C−F, the effects of the induced H−C moments upon the halogens being disregarded in the calculation. As this neglected effect raises the apparent values for the carbon-halogen bond moments, these may reasonably be rounded off to about 1.0 for C−Cl and 0.8 for C−F. A more accurate calculation of these values is impossible because of their great dependence upon the unknown location of the point at which the polarizability of the H−C bond may be supposed to act. The use of these values in the calculation of the $CFCl_3$ moment gives, instead of 1.2, a value of 0.44 as compared to the observed 0.45.

These lower carbon-halogen bond moments may be used equally well in calculating the moments of CH_2Cl_2, $CHCl_3$, etc., because their inductive effects upon the H−C bonds bring the total resultant moments up to the same magnitude as those obtained by using methyl halide moments for the bond moments. It is somewhat disconcerting, at first, to find the use of these much smaller bond moments necessary in some cases, but consideration of the nature of a bond moment makes it clear that its apparent value cannot be constant under all conditions. The system of charges constituting a carbon-halogen group cannot be isolated from the rest of the molecule, and, unless we could determine exactly a point in the system where its moment could be regarded as acting and, similarly, a location for its polarizability, nothing would be gained by

TABLE IV. *Lowering of carbon-halogen moment* ($\times10^{18}$).

C−Cl by C−Cl	0.36	C−F by C−Cl	0.11
C−Cl by C−F	0.56	C−F by C−F	0.21

this process of isolation. A bond moment is merely a measure of the electrical unsymmetry of a certain section of a molecule and is affected by the environment of the section. If the immediate environment of the section in different molecules is the same, the bond moment remains constant; if it is different, the electrical unsymmetry of the section and its moment changes. For example, we may think of the carbon tetrachloride molecule as resolved into four equal C−Cl moments, which, because of the symmetry of the molecule, cancel one another to give zero resultant moment. Each C−Cl moment consists of the moment due to an inherent unsymmetry in the distribution of charge plus the moments induced by each of the three other C−Cl moments. In methyl chloride, the C−Cl moment contains the components in the C−Cl line of the moments induced by the H−C moments, which consist of a possible permanent moment plus the moment induced by the C−Cl moment. As only the roughest kind of separation of these effects can be made, it is as well to treat the entire moment of the molecule as the C−Cl moment. Attachment of more carbons to the methyl carbon gives molecules of somewhat increased moment because of induction,[1] but the effect is noticeable through only two carbons of a chain. Little error will arise from treating the moment of the $-CH_2Cl$ group as a C−Cl moment equal to that of methyl chloride. In chlorobenzene, the immediate environment of the C−Cl is different from that in an alkyl chloride and the moment is somewhat different. If two C−Cl's are separated from one another as in *p*- or *m*-dichlorobenzene, the moment of chlorobenzene may, with little error, be used as a C−Cl bond moment to calculate the resultant moment of the disubstituted molecule. However, in *o*-dichlorobenzene, each C−Cl bond moment is affected by the proximity of the other, not only through direct inductive effects of one C−Cl upon the other, but also through the effects upon the other adjacent parts of the molecule. The very approximate calculation by Smallwood and Herzfeld of the alteration in moment produced by these effects was possible because it was not large. From a practical point of view, the most useful procedure is to assign to one bond the moment of an entire simple molecule containing but one polar group, but it must be born in mind that, when the immediate environment of a bond moment changes, the moment may change.

The moment of $CFCl_3$, which has been calculated in our previous discussion, makes an excellent starting point for the consideration of the moments in Table III. In the following equations, the formula of a molecule or of a bond enclosed in parentheses will represent its moment. The different bond moments are exposed to somewhat different inductive effects in the different molecules, but, as the total resultant moments of the molecules are not large, it is evident that the differences in inductive effects, which, in most cases, partially cancel one another, may commonly, as an approximation, be neglected. Since, however, the C−F bond in methyl fluoride is not exposed to the inductive action of other carbon-halogen bonds, one would expect the values calculated by Eqs. (12) and (14) to be lower than the moment of methyl fluoride. The moment of $CFCl_3$ lies in the C−F line and is given by

$$\begin{aligned}(CFCl_3) &= (C-F)-3(C-Cl)\cos 70^\circ \\ &= (C-F)-(C-Cl) = 0.45, \end{aligned} \quad (5)$$

since $\cos 70^\circ = 1/3$. The moment of CF_2Cl_2 must lie in the line which bisects the F−C−F angle and also the Cl−C−Cl angle and is given by

$$\begin{aligned}(CF_2Cl_2) &= 2(C-F)\cos 55^\circ - 2(C-Cl)\cos 55^\circ \\ &= 1.15[(C-F)-(C-Cl)]. \end{aligned} \quad (6)$$

Substituting for $[(C-F)-(C-Cl)]$ its value given by Eq. (5),

$$(CF_2Cl_2) = 1.15\times 0.45 = 0.52, \quad (7)$$

as compared to an observed value 0.51.

As an approximation, the moment of $CHFCl_2$ may be regarded as lying in the H−C line. Consequently,

$$\begin{aligned}(CHFCl_2) &= (H-C) \\ &\quad +(1/3)[(C-F)+2(C-Cl)]. \end{aligned} \quad (8)$$

A similar approximation gives

$$\begin{aligned}(CF_2Cl_2) &= (C-F) \\ &\quad -(1/3)[(C-F)+2(C-Cl)]. \end{aligned} \quad (9)$$

Adding (8) and (9),

$$(CHFCl_2)+(CF_2Cl_2) = (H-C)+(C-F), \quad (10)$$

but

$$(H-C)+(C-F)=(CH_3F)=1.81 \text{ (obs.)}, \quad (11)$$

and

$$(CHFCl_2)+(CF_2Cl_2)=1.29(\text{obs.})+0.51(\text{obs.})=1.80. \quad (12)$$

The excellence of the agreement between the values calculated by (11) and (12) is accidental as is shown by a similar calculation involving chloroform.

$$(CHCl_3)=(H-C)+(C-Cl)=1.05 \text{ (obs.)}. \quad (13)$$

Adding (5) and (13),

$$(CFCl_3)+(CHCl_3)=(H-C)+(C-F), \quad (14)$$

or 0.45 (obs.) + 1.05 (obs.) = 1.50, while (11) gives $(H-C)+(C-F)=1.81$. Subtracting (13) from (8) and rearranging,

$$(CHFCl_2)=(CHCl_3)+(1/3)[(C-F)-(C-Cl)], \quad (15)$$

but $(CHCl_3)=1.05$ and, from (5), $(1/3)[(C-F)-(C-Cl)]=0.15$, consequently,

$$(CHFCl_2)=1.05+0.15=1.20, \quad (16)$$

as compared to the observed value, 1.29.

As an approximation similar to that in (8),

$$(CHF_2Cl)=(H-C)+(1/3)[2(C-F)+(C-Cl)]. \quad (17)$$

Subtracting (13) from (17) and rearranging,

$$(CHF_2Cl)=(CHCl_3)+(2/3)[(C-F)-(C-Cl)], \quad (18)$$

but $(CHCl_3)=1.05$ and, from (5), $(2/3)[(C-F)-(C-Cl)]=0.30$, consequently,

$$(CHFCl_2)=1.05+0.30=1.35, \quad (19)$$

as compared to the observed value, 1.40.

Although the H−C moment cancels in the final calculations with all of these equations, it has been left in the initial equations to make clearer the assumptions. It is evident that the variation of moment among these different fluorochloromethanes agrees extremely well with the predictions of theory. The agreement between the observed moments and those calculated on the assumption of 110° carbon valence angles does not preclude the possibility of widening of the angles in, at least, some of the methanes. Indeed, it seems probable that there is more or less widening of the angles in all of the unsymmetrically substituted methanes, although, in some cases, this may be too small for detection by means of x-ray or electron diffraction. It would appear, however, that induction is much more important than angle widening in determining the moments of the methanes considered in this paper.

The writers wish to express their indebtedness to the National Research Council for a grant-in-aid, which has made this investigation possible.

The Electric Moment as a Measure of the Ionic Nature of Covalent Bonds

J. GILBERT MALONE, *Department of Chemistry, University of Michigan*

(Received January 13, 1933)

The two-electron bond with hydrogen is found to have the following values of $\mu\times10^{18}$: H−As 0.10; H−P 0.36; H−I 0.38; H−S 0.63; H−Br 0.78; H−Cl 1.03; H−N 1.04; H−O 1.32. These values are believed to give the positions of the elements on an electronegativity scale which is shown to be similar to that prepared by Pauling. The reported moments for inorganic halides as well as the unpublished measurements of A. L. Ferguson and M. G. Malone, giving $\mu=3.1\times10^{-18}$ for $SbCl_3$ and $\mu=2.4\times10^{-18}$ for $SbBr_3$, give fair agreement in most cases with those calculated from the above scale. On the basis of calculated values appreciable moments are predicted for all trihalides of the fifth-group elements except PI_3 and NCl_3 which should give close to a zero moment.

THE idea that the electric moment bears some relation to the ionic quality of the two-electron type of bond has been known for a number of years. It is true that the terms used in describing a bond have been loosely applied, and it is uncertain in some cases just what meaning has been intended. Noyes[1] has clearly described, however, the two-electron bond as potentially polar when it possesses a dipole moment. The qualitative relationship, that atomic bindings between like atoms do not possess moments while those between unlike atoms may do so, is generally known.[2]

The author undertook some six months ago the task of assigning electric moments, derived from the measured moments of molecules to individual bonds. The result of this work was the arrangement of the elements on what Pauling[3] has since called an electronegativity scale. In this early attempt, the scale was built around carbon as a reference. The result was neither as consistent nor as useful as was hoped for.

Certain qualitative regularities did appear, however, among the halides of the fifth-group elements. These will be discussed at more length in light of the fuller knowledge of the subject. The ideas herein involved were of sufficient interest to induce A. L. Ferguson and M. G. Malone to undertake experimental determinations of the electric moments of this group of elements.

It was the belief of the author that any scale which measures the bond differences of atoms should relate to the scale based on electric moments by a constant factor. Attempts to prepare such a scale from independent data were fruitless. At this time the paper of Pauling,[3] giving an electronegativity scale based on thermal data appeared. Since the scale given by Pauling used hydrogen as the point of reference, the author revised his scale to read from the same reference.

The revision of the scale resulted in marked improvement. The factor relating the two scales appeared to be 10^{-18}, but certain difficulties remain. The recent paper by Smallwood,[4] in which a like correlation has been made, induces the author to point out his correlation and certain ways in which it may be applied.

Table I lists the values of the coordinates for the various elements on the two electronegativity scales. The $\Delta^{\frac{1}{2}}$ values are taken from Pauling's[3] paper. He has calculated these values from the increment Δ, of observed bond energy in excess of calculated bond energy. In the latter case, the additivity of the energies of normal covalent bonds has been assumed.

The μ values have been calculated from the observed electric moments of the hydrogen compounds. The moment of the molecule is directly that of the bond in the case of the

[1] W. A. Noyes, J. Am. Chem. Soc. **50**, 2902 (1928).

[2] Ruark and Urey, *Atoms Molecules and Quanta*, McGraw-Hill, 1930; Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932; Glasstone, *Recent Developments in Physical Chemistry*, Blakiston, 1931.

[3] Linus Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[4] Zeits. f. physik. Chemie **B19**, 242 (1932).

TABLE I. *Coordinates of elements on the two electronegativity scales.*

	$\Delta^{\frac{1}{2}}$	$\mu\times10^{18}$		$\Delta^{\frac{1}{2}}$	$\mu\times10^{18}$
H	0.00	0.00	Br	0.75	0.78
As	—	0.10	Cl	0.94	1.03
P	0.10	0.36	N	0.95	1.04
I	0.40	0.38	O	1.40	1.32
C	0.55	—	F	2.00	—
S	0.43	0.63			

hydrogen halides, and since hydrogen is taken as the point of reference the value of the moment fixes the position of the halogen on the electronegativity scale. In the case of oxygen and sulfur the values can be calculated only with a knowledge of the bond angles. The 90° angle taken, places the O−H bond at 1.32 on the scale in good agreement with the value given by Pauling. The position of sulfur at 0.63 is not in accord with the $\Delta^{\frac{1}{2}}$ value of 0.43. Pauling has accepted the tandem structure for S_2Cl_2 in determining the position of sulfur. There is evidence against this structure.[5] Objection has also been raised against the tandem structure for hydrogen peroxide.[6] The value given by Pauling for the O−O bond would be substantially the same, however, if obtained from other sources.

In the case of the fifth-group elements considerable data are obtainable regarding the bond angle.[7] Somewhat arbitrarily the angles 100°, 98°, 96° and 94° have been assumed by the author as the bond angles of N−H, P−H, As−H and Sb−H, respectively. 100° is probably too low for ammonia, but it is nearer the true value than the 90° angle assumed by Smallwood. The decrease in the angles as one proceeds to higher weights is in line with the views of Pauling.[8]

The position of carbon will not be given at this time as it presents difficulties. The substituted halides of methane follow no discernible pattern. Whether the difficulties arise from special properties of carbon, or from the circumstance that in every polar compound of carbon involving bonds of this type at least three species of atoms are included, is not known, but the latter appears the more probable. To use varying bond angles or induced polarization as an explanation is to defeat the purpose of this report. The electric moment values of the mixed halides of the fifth-group elements would furnish highly desirable information in this connection.

The consistency of the electronegativity scale is indicated by the following moments of molecules calculated from bond moments taken from Table I and the bond angles previously used. The moment of the Sb−H bond has been assumed to be zero in calculating values for the antimony halides.

From several viewpoints, it would be desirable to have electric moment data on the compounds resulting from the reaction of the halides with each other as these offer values for the group moments independent of any bond angle. The $\mu\times10^{18}$ values calculated for the halides of the fifth group and recorded in Table III also possess

TABLE II. *Comparison of calculated and measured electric moments.*

Molecule	$\mu\times10^{18}$ Calculated	Measured	Authority
SCl_2	0.51	0.56	J. W. S.[9]
PCl_3	0.98	0.8	B. & E.[10]
		0.9	J. W. S.[11]
PBr_3	0.62	0.61	B. & E.
$AsCl_3$	1.44	1.97	B. & E.
$AsBr_3$	1.05	1.66	B. & E.
$SbCl_3$	1.72	3.1	F. & M.[12]
$SbBr_3$	1.31	2.4	F. & M.
SbI_3	0.62	0.4	See reference 13

[5] Matossi and Aderhold, Zeits. f. Physik **68**, 683–95 (1931).

[6] Maass, Can. J. Res. 781 (1932).

[7] L. Pauling, J. Am. Chem. Soc. **53**, 1380 (1931); Wierl, Ann. d. Physik **8**, 521 (1931); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); D. S. Villars, Chem. Rev. **11**, 369 (1932).

[8] L. Pauling, J. Am. Chem. Soc. **53**, 1380 (1931).

[9] J. W. Smith, Proc. Roy. Soc. **A138**, 154 (1932).

[10] Bergmann and Engels, Zeits. f. physik. Chemie **B13**, 232 (1931).

[11] J. W. Smith, Proc. Roy. Soc. **A136**, 256 (1932).

[12] A. L. Ferguson and M. G. Malone, unpublished measurements.

[13] The value of 0.4×10^{-18} is listed by Smyth (*Dielectric Constant and Molecular Structure*) for SbI_3. He attributes the value to Werner, Zeits. f. physik. Chemie **B4**, 371 (1929). Werner did not measure this compound but quotes the value from Williams, Phys. Zeits. **29**, 684 (1928). Williams and Allgeier, J. Am. Chem. Soc. **49**, 2416 (1927) made an unsuccessful attempt to measure SbI_3 in benzene. The value 0.4×10^{-18} is doubtless too low.

TABLE III. $\mu \times 10^{18}$ *values for the halides of the fifth-group elements.*

	Sb	As	P	N
F_3	≈4	≈3	≈2	≈1
Cl_3	1.7	1.44	0.98	0.0
	(3.1)	(2.0)	(0.85)	
Br_3	1.3	1.05	0.62	0.36
	(2.4)	(1.66)	(0.6)	
I_3	0.62	0.43	0.0	0.92
	(0.4)			

considerable interest. Where measured values are known they are given in parentheses just below the calculated values.

In view of the discrepancy between calculated and measured values, the predicted moments may be given only a semi-quantitative significance. That the minimum moment of the iodides is indicated for the phosphorous compound and not the nitrogen, as hasty consideration might have indicated, illustrates a use of the electronegativity scale. Similarly, the moment of the halogen compounds with nitrogen will increase in the order chloride, bromide, iodide instead of decreasing as occurs in the other columns.

The perfection of two independent measures of electronegativity, one based on thermal data and one on dipole moment data, would be of considerable value. Not only would one supplement the other where experimental values were incomplete, but from the complete scales bond angles in polyatomic atoms might be determined. Before this can be done a clearer definition of electronegativity must be given.

The author expresses his appreciation to A. L. Ferguson and M. G. Malone for the use of data not yet published in the usual way. Dr. Ferguson has also encouraged the writer to present this work at this time.

The Dipole Moments and Structures of Certain Long-Chain Molecules

C. P. SMYTH AND W. S. WALLS, *Princeton University*

(Received December 30, 1932)

The dipole moment of isoprene is measured and found to differ so little from zero that it cannot play a part in the tendency of the substance to polymerize. The moments of hexamethylene and nonamethylene bromide are determined and that of trimethylene bromide is redetermined. Consideration of these values with those previously measured for other long-chain dibromides indicates that the moment of trimethylene bromide may be increased by the existence of a van der Waals attractive force between the two bromine atoms. The orienting effect of the two C−Br dipoles upon one another becomes negligibly small when the carbon chain between them is lengthened from six to nine atoms. The results are best explained by the supposition that the carbon chain is an extended zigzag structure which is not infrequently bent by rotation around one or more C−C bonds.

SINCE the completion of two series of measurements of the dipole moments of polymethylene bromides,[1] Professor C. S. Marvel of the University of Illinois has very kindly lent us samples of hexamethylene bromide and nonamethylene bromide, which are here used to fill the two most important gaps left in the data on the polymethylene bromides. Because of the importance of isoprene in the building up of complex molecules, it seems not inappropriate to include measurements on it with those on the two long-chain molecules. Through the kindness of Dr. Thomas Midgley, Jr., and of Dr. Albert L. Henne, a sample of isoprene prepared by the latter was obtained for the measurements. As a check upon the earlier work, trimethylene bromide was measured in heptane solution.

Purification of Materials

Heptane

Heptane was obtained as in earlier work.[2]

Isoprene

Isoprene was obtained from Dr. Albert L. Henne of Ohio State University as a mixture of 60 percent isoprene with amylenes. For its molecular weight a weighted mean, 68.87, was used. n_D^{25} 1.40995.

Trimethylene bromide

The material used was some of that purified for earlier work,[1] possessing the same refractive index as at the time of the earlier measurements.

Hexamethylene bromide

A somewhat impure sample, b.p. 92–93° (3 mm) kindly lent by Professor C. S. Marvel of the University of Illinois was twice fractionally distilled under reduced pressure. After this material had been used for solutions the solvent was distilled off and the residual hexamethylene bromide was twice fractionally distilled under reduced pressure. A small sample of the middle fraction was used for making additional solutions, the polarizations of which checked those obtained for the first sample.

Nonamethylene bromide

A pure sample, b.p. 127–129° (7 mm) obtained from Professor Marvel was fractionally distilled slowly under reduced pressure, the middle fraction distilling at 103–105° (2 mm) being collected; n_D^{20} 1.49521.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the nonpolar were measured with the apparatus and methods previously employed,[3] a wave-length of 1000 meters being used in the dielectric constant de-

[1] C. P. Smyth and S. E. Kamerling, J. Am. Chem. Soc. 53, 2988 (1931); C. P. Smyth and W. S. Walls, ibid. 54, 2261 (1932).

[2] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. 54, 1854 (1932).

[3] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. 53, 527 (1931).

terminations. In Table I the first column gives the mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25° and 50° of the dielectric constants ϵ, the densities d of the solutions and the polarizations P_2 of the polar substance. The values given opposite $c_2=0$ are those for the solvent. P_2 has been extrapolated to $c_2=0$ in the usual manner to obtain P_∞, from which the moment is calculated as $\mu=0.0127\times10^{-18}[(P_\infty-MR_D)T]^{\frac{1}{2}}$. MR_D, the molar refraction for the D sodium line, was determined directly for isoprene and trimethylene bromide and, for the two long-chain bromides, was calculated as the sum of the atomic refractions. The values of these quantities are given in Table II, and, in Table III, the moments obtained for these dibromides are listed with those previously obtained by Smyth and Kamerling for ethylene bromide and by Smyth and Walls for the higher dibromides.

TABLE I. *Dielectric constants, densities and polarizations.*

c_2	ϵ 25°	d 25°	P_2 25°
Heptane-isoprene (60%)+amylenes (40%) (Mean $M=68.87$).			
0.00000	1.920	0.6795	$(34.58=P_1)$
0.32132	1.959	.6770	27.27
0.44984	1.978	.6760	27.29
0.73520	2.028	.6737	27.30
1.00000	2.087	.6715	27.28

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
Heptane-trimethylene bromide.						
0.00000	1.920	1.883	0.6795	0.6577	(34.58	$34.62=P_1$)
.03248	2.025	1.978	.7089	.6865	114.0	109.1
.07650	2.178	2.114	.7499	.7267	113.0	107.7
.13707	2.406	2.314	.8080	.7836	111.0	105.5
.18568	2.603	2.490	.8563	.8312	109.0	104.1
Heptane-hexamethylene bromide.						
0.03148	2.065	2.014	0.7106	0.6884	162.0	155.0
.06780	2.239	2.174	.7467	.7239	158.9	153.6
.10946	2.447	2.365	.7877	.7643	155.9	151.5
.13438	2.579	2.485	.8123	.7886	154.8	150.2
(Middle fraction of recovered hexamethylene bromide.)						
0.02898	2.054	2.004	0.7082	0.6860	162.6	155.4
.05828	2.195	2.130	.7371	.7144	160.9	153.7
.05841	2.196	2.131	.7374	.7147	160.8	153.8
Heptane-nonamethylene bromide.						
0.02368	2.041	1.994	0.7033	0.6816	191.3	184.5
.04631	2.159	2.101	.7255	.7035	189.8	183.2
.06669	2.262	2.195	.7452	.7229	186.5	180.4
.09153	2.393	2.313	.7689	.7464	184.6	178.4
.09891	2.429	2.346	.7757	.7532	183.3	177.3

TABLE II. *Refractions, orientation polarizations and electric moments.*

	MR_D	$P_\infty-MR_D$ 25°	$P_\infty-MR_D$ 50°	$\mu\times10^{18}$ 25°	$\mu\times10^{18}$ 50°
Isoprene (60%)+amylenes (40%)	25.41	1.87		(0.3)	
Trimethylene bromide	31.2	84.8	79.0	2.02	2.03
Hexamethylene bromide	45.3	119.0	111.4	2.39	2.41
Nonamethylene bromide	59.3	135.2	128.2	2.55	2.58

TABLE III. *Dipole moments of polymethylene bromides.*

Compound	Formula	Solvent	$\mu\times10^{18}$ 25°	$\mu\times10^{18}$ 50°
Ethylene bromide	$Br(CH_2)_2Br$	Heptane	1.02	1.05
Ethylene bromide		Benzene	1.50	1.52
Trimethylene bromide	$Br(CH_2)_3Br$	Heptane	2.02	2.03
Trimethylene bromide		Benzene	1.97	1.98
Tetramethylene bromide	$Br(CH_2)_4Br$	Heptane	1.96	2.01
Tetramethylene bromide		Benzene	2.00	2.03
Pentamethylene bromide	$Br(CH_2)_5Br$	Benzene	2.25	2.28
Hexamethylene bromide	$Br(CH_2)_6Br$	Heptane	2.39	2.41
Nonamethylene bromide	$Br(CH_2)_9Br$	Heptane	2.55	2.58
Decamethylene bromide	$Br(CH_2)_{10}Br$	Benzene	2.54	2.56

DISCUSSION OF RESULTS

Although the formula of isoprene, $CH_2=CH\cdot C(CH_3)=CH_2$, gave reason to expect a moment too small to detect by means of measurements on the liquid, it seemed desirable to establish beyond all doubt that its ease of polymerization was not caused by the moment of the molecule as a whole. The apparent mean moment, 0.3×10^{-18}, found for the mixture of isoprene and amylenes is so small that it may arise entirely from neglect of the atomic polarization. The fact that propylene[4] and α-butylene[5] have moments of 0.37×10^{-18}, while ethylene[5] has zero moment, shows that the double bond itself has no dipole moment, although it may give rise to a moment if unsymmetrically placed in a molecule. The maximum moment to be expected of an amylene is evidently about 0.4×10^{-18} and the mixture would, doubtless, have a decidedly smaller moment. The experimental result shows

[4] K. B. McAlpine and C. P. Smyth, unpublished measurements.

[5] C. P. Smyth and C. T. Zahn, J. Am. Chem. Soc. **47**, 2501 (1925).

a mean moment for the isoprene-amylene mixture between 0 and 0.3×10^{-18} and, therefore, a moment for isoprene lying between approximately the same limits, as would be predicted from the fact that the small moments arising from the double bonds at each end of the molecule would partially cancel one another. It is evident, therefore, that the dipole moment of the molecule is too small to play any appreciable part in the tendency toward polymerization.

The moment of a polymethylene bromide molecule may, as a fair approximation, be regarded as the resultant of the moments in the two C−Br lines and is thus dependent upon the mutual orientation of these bonds. The difference between the moment of ethylene bromide in heptane and in benzene has been attributed to the weakening by the benzene of the forces between the two C−Br dipoles, which, by lessening the potential energy between the dipoles, permits of their turning about the C−C axis farther out of the trans position.[6]

The large energy due to the close proximity of the bromine atoms in the small molecule tends to keep the dipoles near this trans position, thus causing the moment of ethylene bromide to be much lower than the moments of the longer dibromides. Since, in the cases of trimethylene and tetramethylene bromide, the moments are almost the same in the two solvents, it appears safe to neglect the difference of solvent in the case of the longer molecules, where the effect of solvent should be even less. It was shown in the earlier work that, with one exception, the moments could be satisfactorily explained by the assumption of freedom of rotation about all the C−C bonds to give a great variety of forms to the molecules, those forms in which the dipoles point more or less in the same direction being less probable in the shorter molecules and the moments, consequently, being smaller than the calculated values, the difference between observed and calculated values lessening as increasing length of the chain lessens the mutual potential energy of the two dipoles. However, the closeness of the moment of tetramethylene bromide to that of trimethylene bromide was not accounted for by this explanation. It was pointed out that, if the carbon chain retained a rigid zigzag structure with freedom of rotation only about the end C−C bonds, the molecules with an even number of carbon atoms in the chain should have a moment 0.1×10^{-18} lower than those with an odd number of carbons. This would reduce the rise in moment from the three-carbon to the four-carbon compound caused by increasing separation of the two dipoles and thus keep the values close together. In similar fashion, the moments of the five- and six-carbon compounds should be close together, but the moment of hexamethylene bromide, now available to test the hypothesis, is decidedly higher than that of pentamethylene bromide. Because of its greater length, the six-carbon chain offers greater opportunity for some departure from the rigid zigzag structure than does the four-carbon chain, but the marked difference between the moments of the five- and six-carbon compounds renders improbable an explanation of the closeness of the three- and four-carbon values in terms of an alternating effect caused by a rigid zigzag chain.

In our earlier paper, the mutual potential energies of the two dipoles in the different molecules were considered, but discussion of the energies due to other interatomic forces was postponed. Eyring[7] has treated such forces in calculating the dependence of the potential energy of the ethane molecule on rotation about the C−C bond. In the present case, in addition to the forces between the dipoles, which affect their positions relative to one another in such a way as to reduce the resultant moment, there is a repulsive potential, such as $R^n\epsilon^{-\beta R}$, which vanishes for distances R appreciably greater than kinetic theory diameters and a van der Waals potential, $-C/R^6$, which gives rise to attraction.

The constant C for an atom is easily calculated by the method of London.[8] In trimethylene bromide, rotation around the two C−C lines, which make an angle of 110° with each other, would cause the distance between the bromine nuclei to vary from about 6A down to that of the

[6] C. P. Smyth, R. W. Dornte and E. Bright Wilson, Jr., J. Am. Chem. Soc. **53**, 4242 (1931).

[7] H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

[8] F. London, Zeits. f. physik. Chemie **(B) 11**, 222 (1930).

closest possible approach of the two atoms to each other. If the two atoms lay in the same plane on the inside of the C−C−C angle, the nuclear separation of the two bromines would be only 1.53A. As this distance is considerably smaller than the diameter of a bromine atom,[9] it is evident that this position and positions close to it are impossible in the trimethylene bromide molecule. As these are positions in which the two dipoles are not far from pointing in the same direction and thus giving a large moment to the molecule as a whole, it is evident that the moment observed for the molecule will be considerably smaller than that calculated on the assumption that all positions of rotation around the two C−C lines are equally probable. On the other hand, when the internuclear separation is a little greater than the kinetic theory diameter for the bromine atom, the van der Waals potential will become more important than the repulsive potential and there will be an attractive force between the bromine atoms, tending to overcome the repulsion between the dipoles pointing more or less in the same direction. There should, therefore, be a value of the internuclear separation at which the attractive and repulsive forces should approximately compensate one another. The dipoles would then oscillate about this position of minimum potential energy rather than about that in which the two point in opposite directions to give zero moment to the molecule and a minimum dipole potential energy.

The compensation between the repulsive and attractive forces of the bromine atom in the absence of dipole forces is shown by liquid bromine, in which calculation from the density shows that the average volume occupied by a molecule at 0° is equal to that of a cube with an edge of 4.35A. In terms of the dimensions given by Pauling, the Br_2 molecule would be roughly a cylinder of diameter 2.28A with hemispherical ends and total length 4.56A. These dimensions are, of course, decidedly smaller than those given by kinetic theory, from which Smyth and Rogers[10] calculated a diameter 3.2A for the bromine atom. This would extend the hypothetical surface of the molecule calculated from the Pauling dimensions to a distance of 1.6A from the line joining the two bromine nuclei. If the liquid is regarded as made up of molecules of this shape packed parallel to one another in layers, it may be calculated that the average separation of the nearest bromine nuclei in adjacent molecules is about 3.6A. This very rough figure indicates a distance just above which the van der Waals attractive forces should tend to compensate the dipole repulsive forces in trimethylene bromide and give a point of minimum energy for the dipoles. With the bromines at such distances apart in the molecule, the dipoles make such angles with one another as to give considerable resultant moments to the molecules. This should cause the observed moment to be nearer that calculated on the basis of equal probability for all positions of rotation than would be expected in view of the shortness of the carbon chain. In other words, it is not that the tetramethylene bromide moment is low as previously supposed, but that the trimethylene bromide moment is unexpectedly high.

Although the van der Waals attraction may play a part in the tetramethylene bromide molecule, it must be a small part unless the carbon chain is distorted enough by rotation around the C−C bonds to bring the bromines close together. It seems probable that only in trimethylene bromide are the distances between the bromines commonly of such a size as to make the van der Waals attraction between them important. It is also of interest to note that, if the two dipoles in trimethylene bromide are oscillating about a position in which the resultant of their two moments is considerable, increased oscillation accompanying rising temperature will not greatly affect the observed moment. Actually, the values in Table III show a negligible increase in moment from 25° to 50°, and the earlier and less accurate determinations by Smyth and Kamerling showed an apparent increase in moment with temperature decidedly smaller for trimethylene bromide than for pentamethylene.

Since the van der Waals potential varies inversely as the sixth power of the distance, it is negligible in the molecules containing more than

[9] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

[10] C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930).

four carbons unless the ends of the chain are brought close together through rotation around the C−C lines. However, the potential energy between the two dipoles, which varies inversely as the cube of the distance, is still not inconsiderable when they are separated by a rigid zigzag chain of five carbon atoms. In connection with our earlier paper, it was calculated that the potential energy between the two dipoles when both were pointing upward in a sort of cis position was 1×10^{-14} erg greater than when one pointed downward in the opposite direction as in a trans position. As this difference is approximately $1/4\ kT$, it was evident that the trans position of zero moment was the more probable and that the observed moment would still be lower than the calculated and would show some increase with temperature as observed by Smyth and Kamerling. As the separation of the dipoles was approximately doubled in decamethylene bromide, it was evident that the difference between the potential energies of the cis and trans positions was about 1/8 of that in pentamethylene bromide, or about $1/32\ kT$, an energy too small to have any appreciable orienting effect upon the dipoles. In conformity with this, the observed moment was found to differ by less than the uncertainty of the calculation from the value calculated on the assumption of the equal probability of all positions of rotation, and was further found to show little or no variation with temperature.

The approximate validity of the potential energy calculation receives striking confirmation from the additional moments in Table III. The moment of hexamethylene bromide is higher than that of pentamethylene because the dipoles are farther apart and have, therefore, a lower mutual potential energy. However, the difference in potential energy between the cis and trans positions is still not wholly negligible in comparison to kT and is still, therefore, sufficient to make a little less probable the cis positions, which have greater moment, the resultant moment of the molecule, consequently, being somewhat below the calculated value. In nonamethylene bromide, however, the difference in potential energy between the cis and trans positions is so small in comparison to kT as to produce no lowering of the moment, which is practically identical with that of decamethylene bromide and in satisfactory agreement with the calculated value. In the calculation of the resultant moment of the two dipoles, a moment of 1.9×10^{-18} was assigned to each dipole and located in the C−Br line 1.7A from the carbon nucleus. The location of the moments is a rough approximation which makes approximate the calculation of the potential energy between them. In hexamethylene bromide the difference in potential energy between the cis and the trans position is about $1/7\ kT$, which is evidently still sufficient to have a small orienting effect on the dipoles. The difference in nonamethylene bromide drops to about $1/23\ kT$, which, as would be expected, is evidently insufficient to produce detectable orientation.

It must be concluded that the moments in Table III give no positive evidence of an alternating effect such as might be expected if the carbon chain were a rigid zigzag structure, although, in the earlier work, the seemingly low moment of tetramethylene bromide was regarded as an indication of such a structure. However, the small difference, 0.1×10^{-18}, calculated between the molecules with an even-numbered carbon chain and those with an odd would be lessened by any bending of the chain and more or less obscured by the lowering of the moment because of the mutual potential energies of the dipoles and because of inductive effects. Although, as pointed out in the earlier work, the moments do not decide definitely between an extended zigzag carbon chain and one in which free rotation around the C−C bonds gives a great variety of forms to the chain, the results are best explained by the supposition of an extended zigzag chain which is not infrequently bent by rotation around one or more links in the chain.

The Limiting Laws of the Interionic Attraction Theory of Strong Electrolytes

PIERRE VAN RYSSELBERGHE, *Chemistry Department, Stanford University*

(Received December 3, 1933)

The various methods of obtaining the limiting laws of strong electrolytes are briefly discussed. It is shown that the dependence of these limiting laws on the temperature, the dielectric constant of the solvent and the volume of the solution can be deduced from the Gibbs-Helmholtz equation and the virial theorem of Clausius. The Debye-Hückel and the Kramers limiting laws are found to be of the same type as these general limiting laws, with numerical coefficients obtained thanks to the use of the Poisson equation.

INTRODUCTION

THE common features of the various forms of the interionic attraction theory of ionized solutes are: (1) The assumption of complete ionization at low concentrations (sometimes corrected by the consideration of a partial association of ions of opposite signs)[1]; (2) the assumption that the departure from the properties of perfect solutions is entirely due to the Coulomb attractions and repulsions between ions.

The first step in any theory of ionized solutes is either the direct calculation of the correction that has to be introduced in the expression for the free energy of the system on account of those electrostatic forces; or the calculation of the energy involved in the so-called "charging process" of Debye.[2] Either one of these calculations presents difficulties of theoretical and mathematical nature. Milner[3] tried to solve the problem directly by calculating the virial of a mixture of ions but his calculations are extremely intricate and contain a certain number of approximations. The method of Debye and Hückel is based upon the Poisson equation of electrostatics which is only strictly valid for a continuous distribution of electricity. This procedure is rendered uncertain and weak on account of fluctuations, a point discussed by Fowler[4] who considers the Debye-Hückel theory as "empirically successful." The more exact form of the Debye-Hückel theory developed by Gronwall,[5] by Gronwall, La Mer and Sandved[6] and by La Mer, Gronwall and Grieff,[7] although much more satisfactory than the original form of the Debye-Hückel theory, also suffers from fluctuations of an unknown order of magnitude since it is also based on the Poisson equation, for which an exact solution is now obtained. The only parameter of the theory, the mean ionic diameter, is found to have more consistent values than in the original Debye-Hückel theory, where absurdly small or even negative values were often found.

A remarkable solution of the problem, "avoiding the pitfalls of Debye and Hückel's method and the tedium of Milner's" (Fowler) has been obtained by Kramers.[8] It consists of a direct calculation of the correction in the free energy due to the electrostatic forces, by means of Gibb's phase integral. The Poisson equation is not used (at least not as the fundamental point of departure of the theory) and hence fluctuations

[1] N. Bjerrum, Det kgl. danske Vidensk. selskab, Math.-fys. Meddelelser VII, No. 9 (1926); W. Nernst, Zeits. f. Elektrochemie 33, 428 (1927); Zeits. f. physik. Chemie 135, 237 (1928) etc.

[2] P. Debye and E. Hückel, Phys. Zeits. 24, 185 (1923); 25, 97 (1924); E. Hückel, Ergebn. d. exakt. Naturwiss. 3, 199 (1924); W. Orthmann, ibid. 6, 155 (1927).

[3] S. R. Milner, Phil. Mag. 23, 551 (1912); 25, 743 (1913).

[4] R. H. Fowler, *Statistical Mechanics*, pp. 194–197, 316–325, Cambridge, 1929.

[5] T. H. Gronwall, Proc. Nat. Acad. Sci. 13, 198 (1927); Annals of Math. 28, 355 (1927).

[6] T. H. Gronwall, V. K. La Mer and K. Sandved, Phys. Zeits. 29, 358 (1928).

[7] V. K. La Mer, T. H. Gronwall and L. J. Grieff, Phys. Chem. 35, 2245 (1931).

[8] H. A. Kramers, Koninkl. Akad. van Wetenschappen te Amsterdam, Afdeeling Natuurkunde, XXXV, No. 10, 1153 (1926).

are avoided. It is shown that up to definite concentrations depending on the valence type of the electrolyte the part of the free energy due to the electrostatic forces, the activity coefficient and the osmotic coefficient are independent of the size of the ions and the Debye-Hückel limiting laws (under their simplest form, corresponding to negligibly small ionic radii) are obtained for the case of extremely low concentrations. Kramers further shows that the treatment given by Debye and Hückel for higher concentrations (finite size of the ions taken into account) cannot be significant because at those concentrations association takes place and reasonings based on the existence of atmospheres of free ions are invalid. It is to be noticed that the Kramers theory is developed without the use of any parameter. Towards the end of his reasoning, however, Kramers uses the Poisson equation in order to determine the numerical value of a constant.

The object of this note is to show that it is possible to obtain directly the general form of the limiting laws of strong electrolytes from the combined use of the Gibbs-Helmholtz formula and the virial theorem of Clausius. It is then shown that the Debye-Hückel and the Kramers limiting laws are particular forms of these general laws.

Limiting Laws of Perfect Strong Electrolytes

We call "perfect strong electrolyte" a completely ionized solute satisfying the following conditions: (1) The ions are point charges. (2) The departure of the osmotic properties from those of an ideal solution is entirely and only due to the Coulomb forces between the ions. (3) The dielectric constant of the solvent is a function of temperature only.

Let us call $\epsilon_1, \epsilon_2, \cdots \epsilon_i, \cdots$ the charges of the various ions, and $\psi_1, \psi_2, \cdots \psi_i, \cdots$ the electrostatic potentials at the points occupied by the charges $\epsilon_1, \epsilon_2, \cdots \epsilon_i, \cdots$ and due to all the other charges. Thus we have:

$$\psi_i=\frac{1}{D}\left[\frac{\epsilon_1}{r_{1i}}+\frac{\epsilon_2}{r_{2i}}+\cdots+\frac{\epsilon_{i-1}}{r_{i-1,\,i}}+\frac{\epsilon_{i+1}}{r_{i+1,\,i}}+\cdots\right], \quad (1)$$

$r_{1i}, r_{2i}, \cdots r_{ki} \cdots$ being the distances between the various ions and the ion i and D the dielectric constant of the medium. It is obvious that we are dealing with the time averages of the ψ_i's and r_{ki}'s.

The electrostatic energy U_e of the system is given by

$$U_e=\tfrac{1}{2}\textstyle\sum_i \epsilon_i\psi_i. \quad (2)$$

Let us call P the osmotic pressure of the solution, $\bar{P}$ the osmotic pressure of the corresponding ideal solution, A the Helmholtz free energy or maximum work of the system, $\bar{A}$ the same quantity for the ideal solution, V the volume of the solution. We have:

$$P=-(\partial A/\partial V)_T, \quad (3)$$

$$\bar{P}=-(\partial \bar{A}/\partial V)_T. \quad (3')$$

A could be decomposed into $\bar{A}$ and W, the energy involved in Debye's charging process[2]:

$$A=\bar{A}+W. \quad (4)$$

From (3), (3') and (4) we deduce:

$$P=\bar{P}-(\partial W/\partial V)_T. \quad (5)$$

The virial theorem of Clausius leads to the equation of state:

$$PV=NkT+\tfrac{1}{3}\textstyle\sum_i\sum_k r_{ki}\cdot f(r_{ki}), \quad (6)$$

where N is the total number of particles in the volume V, k is Boltzmann's constant, T is the absolute temperature, r_{ki} is the distance between two particles, i and k, $f(r_{ki})$ is the force acting on the particle i on account of particle k. We have:

$$\bar{P}=NkT/V. \quad (7)$$

We deduce from (5), (6) and (7):

$$-(\partial W/\partial V)_T=(1/3V)\cdot\textstyle\sum_i\sum_k r_{ki}f(r_{ki}). \quad (8)$$

From (1) and (2) we find:

$$\textstyle\sum_i\sum_k r_{ki}f(r_{ki})=(1/D)\sum_i\sum_k r_{ki}(\epsilon_i\epsilon_k/r_{ik}^2)$$

or

$$\textstyle\sum_i\sum_k r_{ki}f(r_{ki})=\tfrac{1}{2}\sum_i\epsilon_i\psi_i. \quad (9)$$

Eq. (8) gives then:

$$-(\partial W/\partial V)_T=(1/6V)\cdot\textstyle\sum_i\epsilon_i\psi_i. \quad (10)$$

But since W is the energy spent in charging the ions against the potentials ψ_i, we have:

$$W=\sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i. \tag{11}$$

Eq. (10) becomes then:

$$-\frac{\partial}{\partial V}\left[\sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i\right]=\frac{1}{6V}\cdot\sum_i \epsilon_i\psi_i. \tag{12}$$

We have for the ion i:

$$-\int_0^{\epsilon_i}\cdot\frac{\partial\psi_i}{\partial V}\cdot d\epsilon_i=\frac{1}{6V}\,\epsilon_i\psi_i. \tag{13}$$

Differentiating with regard to ϵ_i:

$$\psi_i=-\epsilon_i\cdot\partial\psi_i/\partial\epsilon_i-6V\cdot\partial\psi_i/\partial V. \tag{14}$$

Integrating:

$$\psi_i=(1/\epsilon_i)\cdot f_1(\epsilon_i/V^{1/6}), \tag{15}$$

$f_1(\epsilon_i/V^{1/6})$ being an arbitrary function of $\epsilon_i/V^{1/6}$.

According to Bjerrum[9] the heat of dilution of an electrolyte is given by:

$$\Delta U=U_e[1+(T/D)\cdot dD/dT]. \tag{16}$$

ΔU is the heat evolved when the solution of volume V is diluted to an infinite volume.

If the solution were perfect, ΔU would be zero. The Gibbs-Helmholtz formula gives:

$$\Delta U=A-T\cdot(\partial A/\partial T)_V. \tag{17}$$

But

$$A=\bar{A}+W. \tag{18}$$

Hence:

$$\Delta U=\bar{A}-T(\partial\bar{A}/\partial T)_V+W-T\cdot(\partial W/\partial T)_V. \tag{19}$$

Since

$$\bar{A}-T(\partial\bar{A}/\partial T)_V=\Delta\bar{U}=0 \tag{20}$$

we obtain

$$\Delta U=U_e\left[1+\frac{T}{D}\cdot\frac{dD}{dT}\right]=W-T\left(\frac{\partial W}{\partial T}\right)_V \tag{21}$$

or:

$$\tfrac{1}{2}\sum_i\epsilon_i\psi_i\left[1+\frac{T}{D}\cdot\frac{dD}{dT}\right]=\sum_i\int_0^{\epsilon_i}\psi_i d\epsilon_i-T\cdot\frac{\partial}{\partial T}\left[\sum_i\int_0^{\epsilon_i}\psi_i d\epsilon_i\right]. \tag{22}$$

For the ion i:

$$\tfrac{1}{2}\epsilon_i\psi_i\left[1+\frac{T}{D}\cdot\frac{dD}{dT}\right]=\int_0^{\epsilon_i}\psi_i d\epsilon_i-T\int_0^{\epsilon_i}\frac{\partial\psi_i}{\partial T}d\epsilon_i. \tag{23}$$

Differentiating with regard to ϵ_i:

$$\left(1+\frac{T}{D}\cdot\frac{dD}{dT}\right)\left(\tfrac{1}{2}\psi_i+\tfrac{1}{2}\epsilon_i\frac{\partial\psi_i}{\partial\epsilon_i}\right)=\psi_i-T\frac{\partial\psi_i}{\partial T} \tag{24}$$

or:

$$\psi_i\left[1-\frac{T}{D}\cdot\frac{dD}{dT}\right]=\epsilon_i\left[1+\frac{T}{D}\cdot\frac{dD}{dT}\right]\cdot\frac{\partial\psi_i}{\partial\epsilon_i}+2T\cdot\frac{\partial\psi_i}{\partial T}. \tag{25}$$

Integrating (D is a function of T only):

$$\psi_i=T^{\frac{1}{2}}D^{-\frac{1}{2}}\cdot f(\epsilon_i/T^{\frac{1}{2}}D^{\frac{1}{2}}) \tag{26}$$

$f_2(\epsilon_i/T^{\frac{1}{2}}D^{\frac{1}{2}})$ being an arbitrary function of $\epsilon_i/T^{\frac{1}{2}}D^{\frac{1}{2}}$. Let us expand expressions (15) and (26) into infinite series, according to Maclaurin's formula. We get:

$$\psi_i=\frac{1}{\epsilon_i}\left[f_1(0)+\frac{\epsilon_i}{V^{\frac{1}{6}}}\cdot f_1'(0)+\frac{1}{2!}\cdot\frac{\epsilon_i^2}{V^{\frac{1}{3}}}\cdot f_1''(0)+\frac{1}{3!}\cdot\frac{\epsilon_i^3}{V^{\frac{1}{2}}}f_1'''(0)+\cdots\right] \tag{27}$$

$$\psi_i=T^{\frac{1}{2}}D^{-\frac{1}{2}}\left[f_2(0)+\frac{\epsilon_i}{T^{\frac{1}{2}}D^{\frac{1}{2}}}\cdot f_2'(0)+\frac{1}{2!}\cdot\frac{\epsilon_i^2}{TD}\cdot f_2''(0)+\frac{1}{3!}\cdot\frac{\epsilon_i^3}{T^{\frac{3}{2}}D^{\frac{3}{2}}}f_2'''(0)+\cdots\right]. \tag{28}$$

One easily finds that $f_1(0)=0$, $f_2(0)=0$, $f_1'(0)=0$. Hence, introducing the Boltzmann constant, so

[9] N. Bjerrum, Zeits. f. physik. Chemie 119, 145 (1926); see W. Orthmann, reference 2, p. 181.

as to make the C's dimensionless:

$$\psi_i = C_1 \frac{\epsilon_i}{DV^{\frac{1}{3}}} + C_2 \frac{\epsilon_i^2}{(kT)^{\frac{1}{2}} D^{\frac{3}{2}} V^{\frac{1}{2}}} + C_3 \frac{\epsilon_i^3}{(kT) D^2 V^{\frac{2}{3}}} + \cdots$$

or:

$$\psi_i = \sum_{m=1}^{m=\infty} C_m \cdot \frac{\epsilon_i^m}{(kT)^{(m-1)/2} \cdot D^{(m+1)/2} \cdot V^{(m+1)/6}}. \tag{29}$$

The C_m's are constants depending on the total number of ions, their valences, etc. Their determination requires calculations of the type of those of Debye and Hückel, of Milner and of Kramers.

In the case of negligibly small ionic radii Debye and Hückel found:

$$\psi_i = -(\epsilon_i/D) \cdot ((4\pi\epsilon^2/DkT) \cdot \sum N_i z_i^2/V)^{\frac{1}{2}}, \tag{30}$$

ϵ being the elementary quantum of electricity, N_i the total number of ions of the kind i, z_i the valence of these ions.

One sees that Eq. (29) reduces to (30) when:

$$C_1 = C_3 = C_4 = \cdots = 0$$

and

$$C_2 = -(4\pi \cdot \sum N_i z_i^2/z_i^2)^{\frac{1}{2}}. \tag{31}$$

The value of W obtained by Kramers is the following:

$$W = \tfrac{1}{2} NkT \ln \omega(x). \tag{32}$$

N is the total number of ions, $\omega(x)$ is a function whose dependence on x is defined as follows:

$$\omega = e^t (1+3t)^{-1}, \tag{33}$$

$$(4\pi/9)x = t^2 (1+3t)^{-3} \tag{34}$$

and

$$x = [(\epsilon^2/DkTN) \cdot \sum N_i z_i^2]^3 \cdot N/V. \tag{35}$$

When x is much smaller than 1, we have:

$$\omega = 1 - (2/3)(4\pi x)^{\frac{1}{2}} - (5/18) \cdot 4\pi x - \cdots, \tag{36}$$

$$-\ln \omega = (2/3)(4\pi x)^{\frac{1}{2}} + \tfrac{1}{2} 4\pi x + \cdots, \tag{37}$$

$$W = -\sum (N_i z_i^2/3) \cdot \epsilon^2 \kappa/D - \cdots \tag{38}$$

with $\kappa = ((4\pi\epsilon^2/DkT) \cdot \sum N_i z_i^2/V)^{\frac{1}{2}}$. The first term of W is the value found by Debye and Hückel for this quantity in the limiting case of negligibly small ionic radii.

Let us calculate ψ_i from (32) and (37). We have:

$$\psi_i = (z_i/\sum N_i z_i^2) \cdot \partial W/\partial \epsilon. \tag{39}$$

This gives:

$$\psi_i = -\frac{\epsilon_i}{D} \cdot \left(\frac{4\pi\epsilon^2}{DkT} \cdot \frac{\sum N_i z_i^2}{V} \right)^{\frac{1}{2}} - \frac{\epsilon_i}{D} \cdot \frac{6\pi\epsilon^4}{(DkT)^2} \cdot \frac{(\sum N_i z_i^2)^2}{NV} - \cdots. \tag{40}$$

Comparing with Eq. (29) we see that:

$$C_1 = C_3 = C_4 = C_6 = \cdots = 0$$

and

$$C_2 = -(4\pi \cdot \sum N_i z_i^2/z_i^2)^2,$$

$$C_5 = -6\pi \cdot (\sum N_i z_i^2)^2/N z_i^4, \text{ etc.} \tag{41}$$

From Eq. (29) we could deduce, if the C_m's were known, the osmotic coefficient g and the activity coefficient f by means of the following relations:

$$g = P/\bar{P} = 1 - (\partial W/\partial V)_T, \tag{42}$$

$$W = \sum_i \left[N_i \sum_{m=1}^{\infty} \frac{C_{i,m} \epsilon_i^{m+1}}{(m+1)(kT)^{(m-1)/2} \cdot D^{(m+1)/2} \cdot V^{(m+1)/6}} \right], \tag{43}$$

$$\ln f_i = (1/kT) \cdot \partial W/\partial N_i. \tag{44}$$

The activity coefficient of the salt ij will be given by:

$$f = [f_i^{\nu_i} \cdot f_j^{\nu_j}]^{1/\nu}, \tag{45}$$

ν_i and ν_j being the numbers of ions i and j into which the salt ij dissociates, ν being the sum of ν_i and ν_j. It is seen that g and f are given by series. If these series are reduced to their first terms, g and f will be given by expressions analogous to those of Debye and Hückel, exactly as in the Kramers theory. This approximation is justified at very low concentrations and for not too small values of D. It happens that these first

terms are also obtained when the Poisson equation is integrated according to the method of Debye and Hückel (hyperbolic sine replaced by its argument), i.e., when in the case of 1−1 electrolytes, for instance, the equation

$$\Delta\psi = -(4\pi n\epsilon/D)(e^{-\epsilon\psi/kT} - e^{\epsilon\psi/kT}) \qquad (46)$$

is arbitrarily replaced by

$$\Delta\psi = 8\pi n\epsilon^2\psi/DkT. \qquad (47)$$

This result cannot be considered as anything more than a coincidence, since La Mer, Gronwall and Sandved[6] have shown that if the exact integration of the Eq. (46) is carried out, the value of ψ_i and hence that of the electrostatic energy of the mixture of ions become infinite when the radius of the ions becomes infinitely small. This would tend to show that the Poisson equation as applied to electrolytes is meaningless in this case.

Summing up we may say that the reasonings developed in this paper show how far it is possible to go in the solution of the problem of electrolytes without using more statistics than what is involved in the virial theorem and without using the Poisson equation. These reasonings also show that, insofar as their dependence on the temperature, the dielectric constant of the solvent and the volume of the solution is concerned, the limiting laws of Debye-Hückel and of Kramers are essentially correct.

Wave Functions for the Ground State of Lithium and Three-Electron Ions

E. BRIGHT WILSON, JR., *Gates Chemical Laboratory, California Institute of Technology*

(Received January 16, 1933)

Improved wave functions and ionization potentials have been obtained for the configuration $1s^2\ 2s$, by using the variation method with a variation function containing four parameters. The wave function for the whole atom is of the determinant form, built up of K and L single-electron functions. The K function used is hydrogen-like with one parameter, the effective nuclear charge, and the L function is of the form $are^{-\eta r}-e^{-\zeta r}$. A simple rule is obtained by means of which it is possible to write down the wave function for any three-electron ion without further calculation. The deviation of the calculated ionization potentials from the observed values is 0.9 percent for Li I and decreases to 0.3 percent for C IV. Comparison is made with the results of other investigators and curves showing the wave functions and electron density functions are given.

INTRODUCTION

THE solution of the Schrödinger equation for the hydrogen atom and for the ground state of the helium atom[1] has been carried out to a high degree of exactness, but the best approximation which has been obtained for the lowest state of lithium is not nearly so accurate. While it is probably not feasible at present to obtain a result for the energy which is superior to the experimental value in accuracy, it was thought worth while to test out on lithium various possible approximate solutions, partly because the better agreement with the experimental energy and the correspondingly improved wave function and electron-density function were considered important in themselves and partly because this study would provide a basis for similar investigations of heavier atoms.

GENERAL METHOD

Slater[2] has shown how to build up a properly antisymmetric wave function for a many-electron atom by using a determinant whose elements are functions of the coordinates of a single electron only. In particular, if the interaction of the electrons with each other is regarded as a perturbation and neglected in obtaining the zeroth order approximation to the solution of the wave equation, there results for lithium:

$$\psi^\circ=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} A_1 & A_2 & A_3 \\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3 \\ B_1 & B_2 & B_3 \end{vmatrix} \tag{1}$$

where A_1 is the $1s$ hydrogen-like wave function with positive spin for the first electron; $\bar{A}_2$ is the same function with negative spin for the second electron, and B_3 is the $2s$ hydrogen-like function with plus spin for the third electron.

The method adopted in this work was to seek a better approximation by the use of new functions for B based on the hydrogen-like functions but generalized by the introduction of parameters whose values were then determined by the application of the variation method.

The solution of the variation problem:

$$\delta E=\delta[\int\psi^* H\psi d\tau/\int\psi^*\psi d\tau]=0, \tag{2}$$

where ψ is the function varied and H is the Hamiltonian operator for the system, is equivalent to solving the wave equation

$$H\psi=W\psi \tag{3}$$

with the usual boundary conditions. In particular if this variation problem is not completely solved but instead a trial function ψ used which contains a number of parameters which are varied until E is a minimum, then it can be shown[3] that E is an upper limit to the energy, and ψ is assumed to be an approximate solution. The method which was used in this problem is

[1] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[2] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[3] C. Eckart, Phys. Rev. **36**, 878 (1930).

applicable to the lowest state of any multiplicity or total angular momentum.

Previous Work on Lithium

Hargreaves[4] has applied the method of Hartree to lithium, but his results have not appeared in a very usable form. Hartree's method of the "self-consistent field" is not based on the variation principle, but Slater[5] has shown the relation between these two procedures and in addition has pointed out that several important corrections are needed before the energy values obtained can be compared with the experimental ionization potentials. The curve Hargreaves publishes for the wave function cannot be used for comparison since he gives no scales and has not made the L function orthogonal to the K function, so that its shape is of little significance. However, he does give a table of the self-consistent field, and these values will be compared with other results in Table III.

Eckart,[3] using essentially the same method as is described in this paper, employed hydrogen-like functions with two parameters, the effective nuclear charges for the K- and L-shells. Thus if we use $a, b, c, \cdots$, to represent single electron-orbit functions without the spin factor and $A, B, C, \cdots; \bar{A}, \bar{B}, \bar{C}, \cdots$, for the same functions with plus and minus spin, respectively, Eckart's solutions are

$$\begin{aligned} &(K\text{-shell functions})\ a = e^{-\xi r} \\ &(L\text{-shell functions})\ b = e^{-\eta r}(\eta r - 1). \end{aligned} \tag{4}$$

There appears to be an error in his energy value for lithium so this has been recalculated and will be found in Table I.

Guillemin and Zener[6] introduced an additional parameter (α) into b, obtaining thereby a considerable improvement in the energy. Their function is:

$$b = e^{-\eta r}(\alpha r - 1) \tag{5}$$

and values for the energy will also be found in Table I and of the parameters in Table II. In addition these authors varied the exponent of r in the coefficient, but found in this case that its best value was one, the hydrogen-like value.

Zener[7] and Slater[8] noted that α is fairly large and concluded that a good result would be obtained with the very simple function

$$b = re^{-\eta r}. \tag{6}$$

Table I. *Energies and ionization potentials (atomic units: e^2/a_0).*

	Total energy	Diff.	%	Ionization potential	Diff.	%
			Li I			
Experimental	−7.4837	—	—	0.1983	—	—
4-Parameter	−7.4192	0.0645	0.86	.1965	0.0018	0.91
Guillemin-Zener	−7.4183	.0654	.87	.1956	.0027	1.36
Slater	−7.4179	.0658	.88	.1953	.0030	1.51
Hydrogen-like	−7.3922	.0915	1.22	.1696	.0287	14.5
			Be II			
Experimental	−14.3422	—	—	.6704	—	—
4-Parameter	−14.2639	.0783	.55	.6663	.0041	.61
Slater	−14.2584	.0838	.58	.6607	.0097	1.45
			B III			
Experimental	−23.476	—	—	1.395	—	—
4-Parameter	−23.363	.113	.48	1.390	.005	.36
Slater	−23.350	.126	.54	1.378	.017	1.22
			C IV			
Experimental	−34.778	—	—	2.3722	—	—
4-Parameter	−34.713	.065	.19	2.3650	.0072	.30
Guillemin-Zener	−34.698*	.080	.23	2.3496*	.0226	.95
Slater	−34.690	.088	.25	2.3422	.0300	1.26

* This is probably not quite the best value obtainable with this function.

Table II. *Parameter values, except for four-parameter function.*

	ξ	η	α	ξ	η	α
	Li I			Be II		
Guillemin-Zener[6]	2.688	0.630	5.56	3.688	1.158	5.88
Slater	2.688	.630	—	3.682	1.09	—
Hydrogen-like[3]	2.686	.888	—	3.70	1.42	—
	B III			C IV		
Guillemin-Zener[6]	4.688	1.671	5.56	5.688	2.179	5.88
Slater	4.676	1.52	—	5.672	1.95	—
Hydrogen-like[3]	4.72	1.96	—	5.71	2.48	—

[4] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929).
[5] J. C. Slater, Phys. Rev. **35**, 210 (1930).
[6] V. Guillemin and C. Zener, Zeits. f. Physik **61**, 199 (1930).
[7] C. Zener, Phys. Rev. **36**, 51 (1930).
[8] J. C. Slater, Phys. Rev. **36**, 57 (1930).

This function was tried and, as is seen in Table I, found to be remarkably good considering its simplicity. It is better than the hydrogen-like function with screening constant used by Eckart, although, of course, not as good as Guillemin and Zener's function, of which it is a special case.

Functions Investigated

The type of function which has been used in this paper, a natural generalization of Guillemin and Zener's function, is

$$b=\alpha re^{-\eta r}-e^{-\zeta r}. \tag{7}$$

The same type has been used by Slater[9] in seeking analytical expressions for Hartree's graphical wave functions. Results which are obtained by using (7) are listed in Table I under the heading "4-parameter" function.

The following form was also tried but found not to give as good results as (7):

$$b=\alpha re^{-\eta r}+re^{-\zeta r}. \tag{8}$$

Since the variation principle is applicable to the lowest P state of the atom, the following function was tried for the configuration $1s^2\ 2p$ of lithium:

$$c=(\gamma e^{-\kappa r}+e^{-\lambda r})r\cos\vartheta. \tag{9}$$

However, the surprising result was obtained, on varying the parameters, that this function reduced to the simple screening constant type used by Eckart. In other words, the best values of the parameters γ, κ and λ were such that $\gamma=0$; $\kappa=\lambda$. Therefore, the calculated total energy for this configuration, $-7.35039\ e^2/a_0$, is not different from Eckart's value, but by combining this with the best calculated value for the ground state, $-7.41915\ e^2/a_0$, a new result for the resonance potential of lithium is obtained, $0.06876\ e^2/a_0$, which is to be compared with the experimental value, $0.06794\ e^2/a_0$. The difference is $0.0082\ e^2/a_0$ or 1.2 percent.

The calculated energy of removal of the $2p$ electron from $1s^2\ 2p$ of lithium is 2.2 percent greater than that for a $2p$ hydrogen atom, $e^2/8a_0$, whereas the experimental value is 4.2 percent greater than $e^2/8a_0$. The discrepancy of 2 percent is probably to be attributed to the effect of polarization of the K-shell by the valence electron, the effect of which is not taken into consideration by any of the variation functions used in this paper, approximate calculations of the polarization energy[10] leading to somewhat larger values than the 2 percent needed. It is of interest that these calculations show, as suggested by Pauling and Goudsmit,[11] that there is appreciable interaction of the valence electron with the core of the atom other than polarization even for "nonpenetrating" orbits.

Details of Method

When the units $a_0=h^2/(4\pi^2\mu e^2)$, $2Rhc=e^2/a_0$ and e are used for length, energy and charge, respectively, Schrödinger's equation for the three-electron problem becomes

$$H\psi=(-\tfrac{1}{2}\nabla^2+V)\psi=W\psi \tag{10}$$

where

$$V=1/r_{12}+1/r_{23}+1/r_{13}-Z/r_1-Z/r_2-Z/r_3. \tag{11}$$

∇^2 is the Laplacian for the coordinates of the three electrons, and Z is the atomic number of the atom or ion. As pointed out by Hylleraas,[12] application of Green's theorem to the term in (2) involving the Laplacian yields for E:

$$E=(M'-2L')/2N' \tag{12}$$

where

$$\left.\begin{aligned} M'&=\int|\text{grad }\psi|^2d\tau\\ L'&=-\int\psi^*V\psi d\tau\\ N'&=\int\psi^*\psi d\tau \end{aligned}\right\}. \tag{13}$$

Further, if the change in scale:

$$r'=\xi r;\quad \eta'=\eta/\xi;\quad \zeta'=\zeta/\xi \tag{14}$$

is made, it is possible to differentiate E with respect to ξ, solve for the minimizing value of ξ and insert this value in E. The result is

$$E=-L^2/2MN \tag{15}$$

where L, M, N differ from L', M', N' only in that the substitutions (14) have been made.

The other parameters enter in such a complicated fashion that it is not feasible to obtain the

[9] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[10] L. Pauling and S. Goudsmit, *The Structure of Line Spectra*, McGraw-Hill, New York, 1930, p. 47.

[11] Reference 10, p. 48.

[12] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

minimum by differentiation so resort was had to actually computing E for various values of the parameters and graphically determining the minimum. This is a tedious process at best; the quickest and most certain method was found to involve constructing rough contour maps of the energy surface. An estimate was first made of the probable values of parameters. One of these (usually η') was inserted in the formula for E and a survey of the ζ', α' plane made by giving ζ' a number of fixed values and plotting E as a function of α'. Each of these curves then gives a section of the energy surface, with E thought of as a function of α' and ζ' only. From these a contour map can be constructed and an estimate made of the best values of α' and ζ' for the value of η' originally chosen. With these values of α' and ζ', η' is then varied until a minimum is found. A contour map may be constructed for the α', ζ' plane with this new value of η' and the best values redetermined.

K-Shell Functions

In all the cases discussed here, with the exception of Hargreave's paper, the function used for the K electrons was the same as in Eckart's work, i.e., a hydrogen-like function with one parameter, the effective nuclear charge, as in Eq. (4). It is well known that this is not the best function to represent the K electrons, some term such as one of those used by Hylleraas,[12] for example, to correct more exactly for the repulsion of the electrons giving a better result. However, the introduction of even the simplest of these interaction factors, such as $(1+\gamma r_{12})$, enormously complicates the problem in the case of lithium and so was not regarded as practicable. Instead, the ionization potential was calculated by subtracting the energy of the Li^+ ion computed by using the same type of $1s$ wave function, the value of the energy so calculated being: 7.22266 e^2/a_0 for Li^+; 13.59766 e^2/a_0 for Be^{++}; 21.97266 e^2/a_0 for B^{+++}; and 32.34766 e^2/a_0 for C^{++++}. Although the total energy of the lithium atom is, therefore, in error by about 0.065 e^2/a_0 or 0.86 percent in all these examples due to the inaccuracy of the K functions, the assumption made that this error is nearly equal in the ion and in the atom is well justified by the close agreement between the experimental and theoretical ionization potentials as given in Table I.

Comparison of L Functions

The $2s$ functions which have been enumerated do not, at first glance, appear to be very similar, and it may seem strange that such different functions can all be even moderately good approximations to the true solution. The reason for the discrepancy is the use of single-electron wave functions for comparison instead of the wave function for the atom as a whole. Slater[9] has pointed out that it is possible to make the $2s$ function orthogonal to the $1s$ function by adding to the $2s$ a certain fraction of the $1s$ function. Since the wave function for the whole atom is a determinant, it possesses the property that the addition of the members of any row multiplied by any factor to the members of any other row does not change the value of the determinant. Thus:

$$\psi=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} A_1 & A_2 & A_3 \\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3 \\ B_1 & B_2 & B_3 \end{vmatrix}=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} A_1 & A_2 & A_3 \\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3 \\ B_1+\beta A_1 & B_2+\beta A_2 & B_3+\beta A_3 \end{vmatrix} \tag{16}$$

and in particular β may be so chosen that

$$\int A_1(B_1+\beta A_1)d\tau=0. \tag{17}$$

With this value of β, the single-electron functions are mutually orthogonal, since A_1 and $\bar{A}_1$ have opposite spins. In addition, the functions a and b later tabulated have been normalized to 4π, i.e.,

$$\int A_1^2 d\tau=\int B_1^2 d\tau=4\pi. \tag{18}$$

The orthogonalization and normalization make a and b unique (as long as functions of different spins are not combined), and it is thus possible to

compare the different approximations which have been obtained.

As shown by Fig. 3, the four approximations already enumerated are remarkably near to each other. The only one showing any great deviation is the hydrogen-like function, which is also the one giving the poorest energy value. The simple, so-called "nodeless" function of Slater[8] is seen to be miscalled, since, when it is orthogonalized, it has a node in practically the same place as the more precise functions.

Results

The parameter values obtained for the functions of Guillemin and Zener, Slater, and Eckart are found in Table II. In the case of the four-parameter function, the best parameter values fit into a very convenient rule if we introduce the idea of screening constants. The function for the L electron which has been used, Eq. (7), consists of two terms (before orthogonalization), and it is seen that the first term is the more important at large distances, because of the factor r and the smaller coefficient in the exponent, while the second term is the more important for small values of r. In the simple hydrogen-like function analogous to this, there is only one exponential, whose exponent is $Z_{\text{eff.}}/2$, or $(Z-\sigma)/2$ if we define the quantity σ, the screening constant. σ thus represents the shielding effect of the inner electrons which reduces the attraction of the nucleus for the L electron. Likewise in our more complicated function the idea of the screening constant can be introduced, only here two different screening constants for the L electron are needed, since there are two exponentials. The results which are obtained are that these screening constants are essentially independent of the nuclear charge and, therefore, provide a convenient method of summarizing the results of the variation problem. Furthermore, to a sufficiently close approximation, the screening constant for the inner part of the $2s$ function is zero, so that in a sense the four parameters originally used have been reduced to three.

The parameter α can also be related for the ions of different atomic number. It is found that in all four cases investigated α' comes so close to 0.5 that it is very convenient to assume that

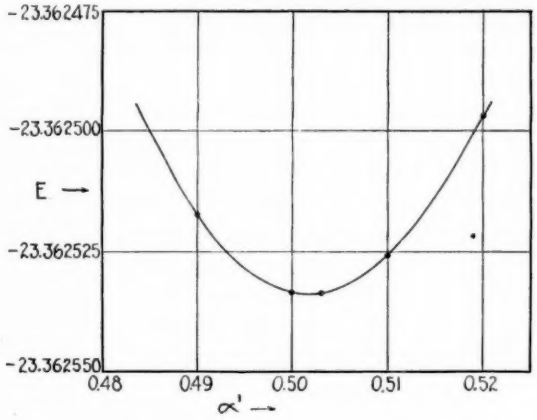

FIG. 1. Curve showing the variation of E with the parameter α' for B III, with the four-parameter function with $\sigma_1=0.31$, $\sigma_2=1.67$, $\zeta=Z/2$.

value for all three-electron ions. Fig. 1 shows the way E varies with α' in the case of B III. Since $\alpha=\alpha'\xi$ and $\xi=Z-\sigma_1$, if σ_1 is the K-shell screening constant, therefore,

$$\alpha=0.5(Z-\sigma_1)=0.5(Z-0.31). \tag{19}$$

Introducing the values indicated above for the parameters η, ζ, α and ξ, we obtain for the best wave function for the state $1s^2\ 2s\ ^2S$ of any three-electron atom or ion the expression

$$\psi=(1/6^{\frac{1}{2}})\textstyle\sum_P \pm PA_1\bar{A}_2B_3. \tag{20}$$

$$a=(\xi^3/\pi)^{\frac{1}{2}}e^{-\xi r} \tag{21}$$

$$b=k\{\alpha re^{-\eta r}-e^{-\zeta r}+\beta e^{-\xi r}\} \tag{22}$$

where

$$\left.\begin{array}{ll}\xi=Z-\sigma_1 & \zeta=Z/2\\ \eta=(Z-\sigma_2)/2 & \alpha=0.5(Z-\sigma_1)\end{array}\right\} \tag{23}$$

$$\beta=8\xi^3\left\{\frac{1}{(\zeta+\xi)^3}-\frac{3\alpha}{(\eta+\xi)^4}\right\}\quad\text{orthogonality constant}$$

$$K=\left\{\pi\left[3\frac{\alpha^2}{\eta^5}+\frac{1}{\zeta^3}+\frac{\beta^2}{\xi^3}-\frac{48\alpha}{(\eta+\zeta)^4}+\frac{48\alpha\beta}{(\eta+\xi)^4}-\frac{16\beta}{(\zeta+\xi)^3}\right]\right\}^{-\frac{1}{2}}$$

and $Z=$ atomic number of ion; and $\sigma_1=0.31$, K-shell screening constant. $\sigma_2=1.67$, L-shell screening constant. The sum in Eq. (20) is over all permutations P of the numbers 1, 2, 3, odd permutations having the negative sign. (This is another

way of writing the determinant of Eq. (1).) The single-electron functions a and b as given above are individually normalized to unity and are mutually orthogonal.

The energies obtained with the various functions are tabulated in Table I, which also contains the calculated ionization potentials. The experimental energy values are listed in the same table, together with deviations and percent deviations of the calculated and observed quantities. It is seen that the poorest values are those obtained with the hydrogen-like function of Eq. (4), even the simpler function put forward by Slater and given in Eq. (6) being considerably better. The error in the ionization potential computed by the use of the four-parameter function is only from thirty to seventy percent of the corresponding error found when Guillemin and Zener's function is used.

Fig. 2 is a plot of the four-parameter single-electron function for the $2s$ electron normalized to 4π and with β adjusted so that the L and K functions are orthogonal. Fig. 3 gives $4\pi r^2 b^2$, the distribution function integrated over all angles. On comparing the size of the two maxima in Li I and in hydrogen ($2s$ state), the effect of the core electrons of lithium in reducing the probability of close approach to the nucleus by the valence electron is clearly seen, in agreement with the old concept of the penetrating orbit, in the inner segment of which the electron was speeded up by the increased effective nuclear charge, diminishing the time spent in traversing this segment. Fig. 4 gives the total electron density function for Li I, integrated over all angles. The very steep rise at the K-shell and the more spread-out maximum of the single L electron are shown.

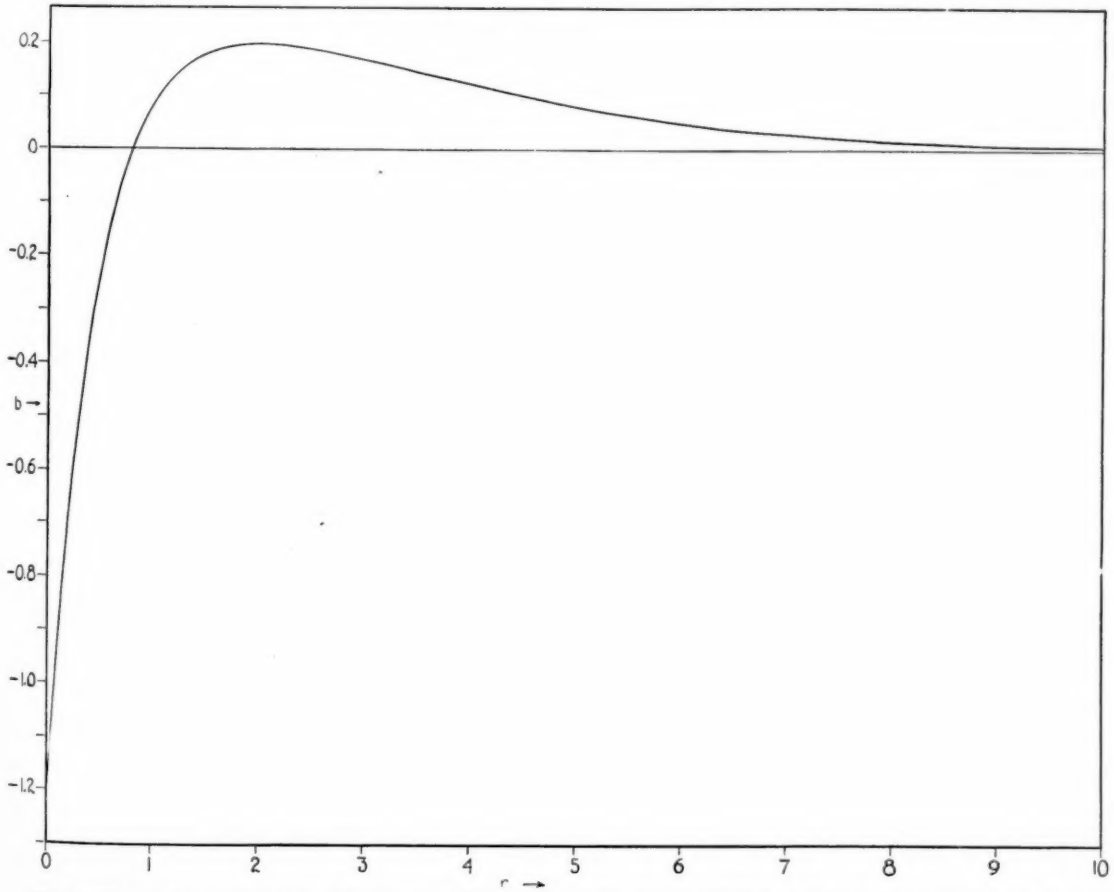

FIG. 2. Plot of four-parameter orthogonalized single-electron wave function b for $2s$ electron, normalized to 4π. r in atomic units. Li I.

The Internal Field

Hargreaves[4] has given a table of values for the self-consistent field for lithium, obtained graphically. This is expressed in terms of the "effective nuclear charge for field," which is the number Z_f such that the charge $Z_f e$ placed at the position of the nucleus would give the same field (not potential) at the point in question as is actually found. In other words:

$$Z_f = r^2(\partial V/\partial r) \qquad (24)$$

in atomic units.

In Table III the values of Z_f found by Hargreaves are listed. In addition there is also given the field due to the nucleus and the two K

Table III. *Field due to K electrons. r in atomic units.*

r	Z_f – Hargreaves	Z_f – Eq. (24)	Difference
0	3	3	0
0.1	2.963	2.965	−0.002
.2	2.807	2.811	− .004
.3	2.559	2.559	.000
.4	2.280	2.272	+ .008
.6	1.773	1.748	+ .025
.8	1.425	1.394	.031
1.0	1.219	1.192	.027
1.2	1.108	1.089	.019
1.4	1.050	1.039	.011
1.6	1.022	1.017	.005
1.8	1.009	1.007	.002
2.0	1.003	1.003	.000

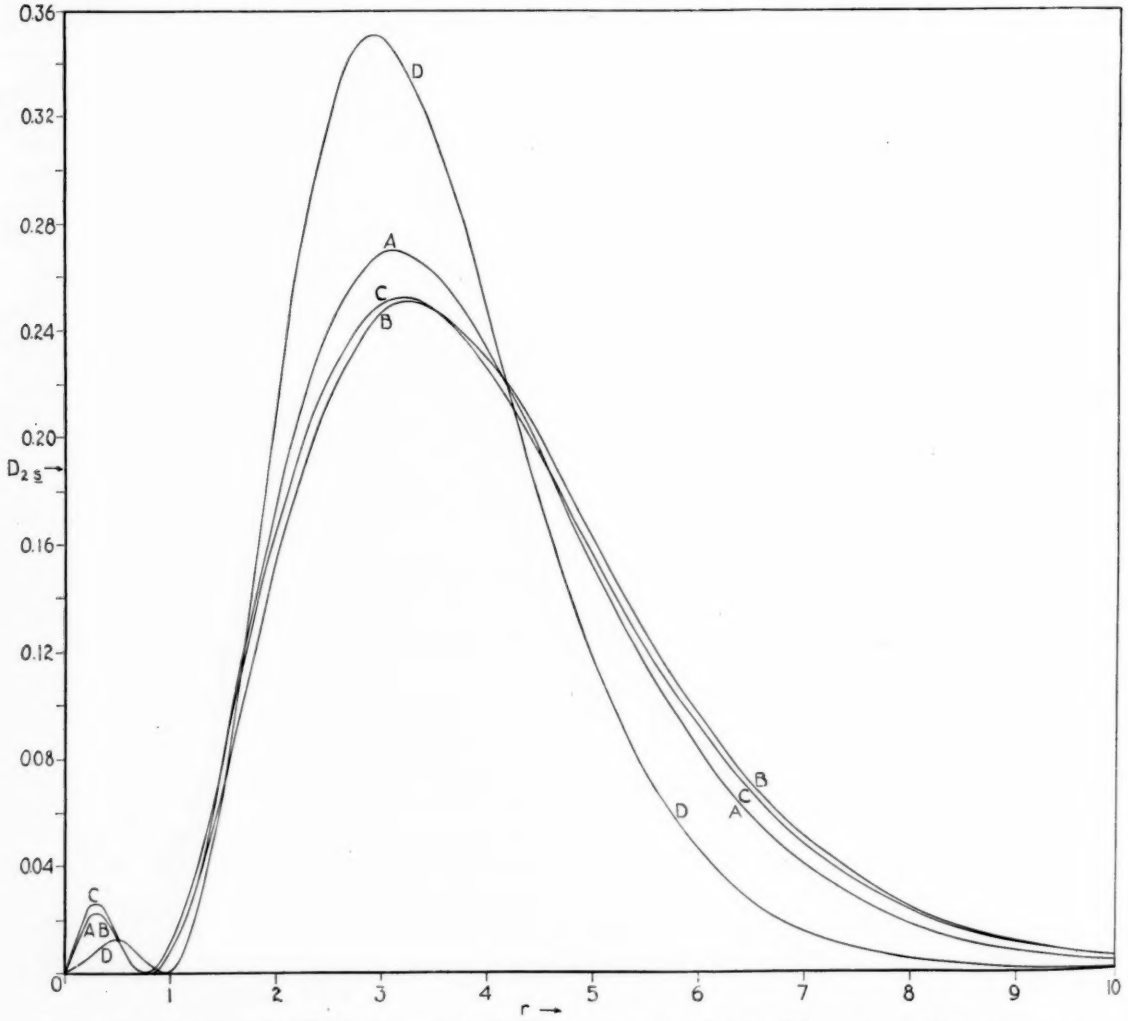

Fig. 3. Plot of electron distribution function for 2s electron, $D_{2s} = 4\pi r^2 b^2$, with different types of functions. Li I. *A*, 4-parameter; *B*, Guillemin-Zener; *C*, Slater; *D*, hydrogen-like.

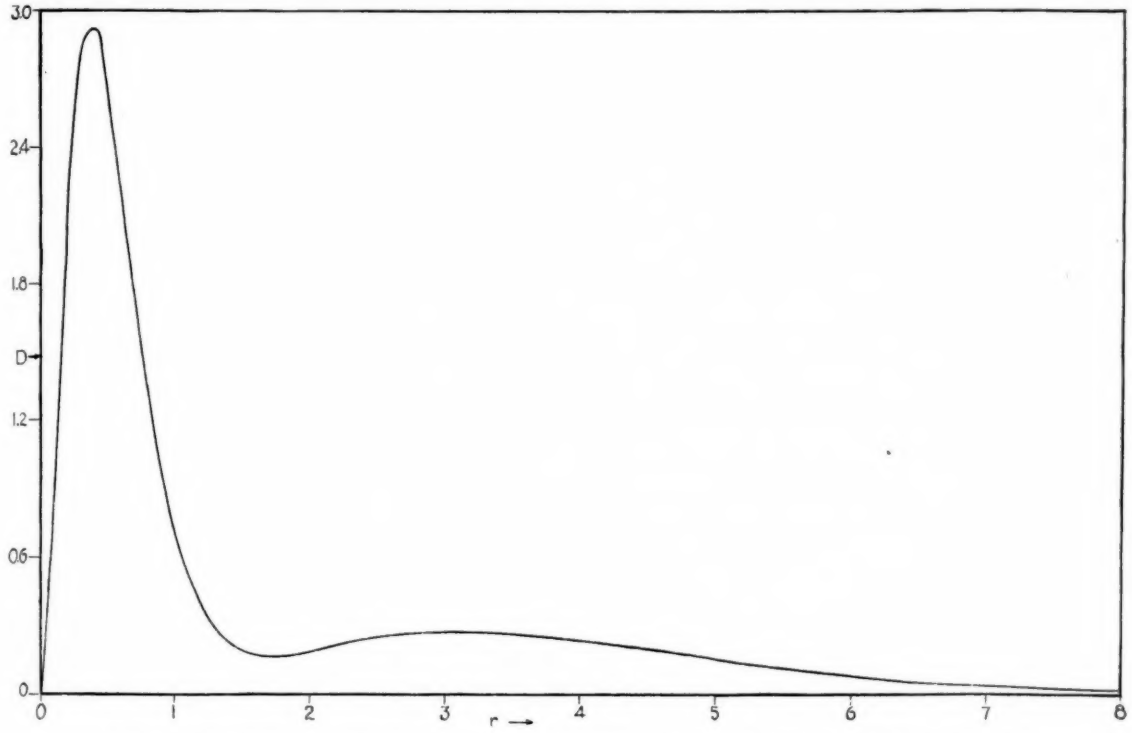

FIG. 4. Total electron distribution function for Li I, $D=4\pi r^2\psi\psi^*$, as a function of r in atomic units.

electrons, found by using the K functions previously described. To calculate this latter quantity at a distance R from the nucleus, use is made of the equation derived from electrostatics for the field due to a distribution of electricity of density $\rho=a^2$

$$V=-\frac{Z}{R}+\frac{8\pi}{R}\int_0^R r^2a^2dr+8\pi\int_R^\infty ra^2dr. \quad (25)$$

If a is given by Eq. (21), (25) becomes

$$V=-Z/R+(2/R)\{1-e^{-2\xi R}(1+\xi R)\}. \quad (26)$$

As is seen from Table III, there is quite good agreement between the field calculated in this manner and that of Hargreaves, the deviation being about 2 percent at most. This comparison refers only to the 1s functions used, and not to the 2s function, however.

EXPRESSIONS FOR N, L, M

Eq. (15) gives the energy in terms of N, L, M, defined by (13). Algebraic expressions for N, L, M for the configuration $(1s)^2\ 2s$ and for the 2s functions of (7) are given below:

$$\alpha'=\alpha/\xi;\quad \zeta'=\zeta/\xi;\quad \eta'=\eta/\xi. \quad (27)$$

$$2K=\zeta'+\eta';\quad b=1+\eta';\quad f=1+\zeta';\quad g=1+K. \quad (28)$$

$$N=\pi^3\left\{\frac{3\alpha'^2}{\eta'^5}-576\frac{\alpha'^2}{b^8}+384\frac{\alpha'}{b^4f^3}-3\frac{\alpha'}{K^4}+\frac{1}{\zeta'^3}-\frac{64}{f^6}\right\}. \quad (29)$$

$$L=\pi^3\left\{3(2Z-\tfrac{5}{8})\frac{\alpha'^2}{\eta'^5}+(1.5Z-3)\frac{\alpha'^2}{\eta'^4}+3\frac{\alpha'^2}{b^4}+6\frac{\alpha'^2}{b^5}+(516-384\cdot Z)\frac{\alpha'^2}{b^7}-576\cdot Z\frac{\alpha'^2}{b^8}-\frac{384\alpha'^2}{b^4(2+b)^3}\right.$$

$$-\frac{1152\alpha'^2}{b^4(2+b)^4}+(4-2Z)\frac{\alpha'}{K^3}-4\frac{\alpha'}{g^3}-6\frac{\alpha'}{g^4}+(128\cdot Z-256)\frac{\alpha'}{f^3b^3}+192Z\frac{\alpha'}{b^4f^2}+(384Z-384)\frac{\alpha'}{b^4f^3}$$

$$+\frac{128\alpha'}{f^3(2+b)^3}+\frac{384\alpha'}{f^3(2+b)^4}+\frac{1536\alpha'}{b^4f^3(2+f)^2}+\frac{1536\alpha'}{b^4f^2(2+f)^3}+\frac{128\alpha'}{f^3(f+b)^3}+\frac{192\alpha'}{f^2(f+b)^4}-3(2Z-\tfrac{5}{8})\frac{\alpha'}{K^4}$$

$$+(2Z-\tfrac{5}{8})\frac{1}{\zeta'^3}+(Z-2)\frac{1}{\zeta'^2}+\frac{2}{f^2}+\frac{2}{f^3}+(20-64Z)\frac{1}{f^5}+(128-64Z)\frac{1}{f^6}-\frac{512}{f^6(2+f)^2}-\frac{512}{f^5(2+f)^3}\Bigg\}. \quad (30)$$

$$M=\pi^3\Bigg\{\frac{6\alpha'^2}{\eta'^5}+\frac{\alpha'^2}{\eta'^3}+384\frac{\alpha'^2}{b^7}-576\frac{\alpha'^2}{b^8}-1152\frac{\eta'\alpha^2}{b^8}-6\frac{\alpha'}{K^4}-3\frac{\zeta'\eta'\alpha'}{K^4}-128\frac{\alpha'}{b^3f^3}+384\frac{\alpha'}{b^4f^3}+2\frac{\alpha'\zeta'}{K^3}$$

$$+384\frac{\alpha'\zeta'}{b^4f^3}+384\frac{\alpha'\eta'}{b^4f^3}+\frac{2}{\zeta'^3}+\frac{1}{\zeta'}-128\frac{\zeta'}{f^6}-64\frac{1}{f^6}\Bigg\}. \quad (31)$$

I wish to express my appreciation of the assistance of Professor Linus Pauling, who proposed this problem and made many useful suggestions during the progress of the work. I am also indebted to Mr. L. G. Bonner for much of the numerical computation.